

Volcanic aggregates and alkali-silica reactions in the world: a comparative study with Azores aiming to enhance concrete durability on volcanic oceanic islands

Tese de Doutoramento

Sara Maria Teixeira de Medeiros

Doutoramento em
GEOLOGIA



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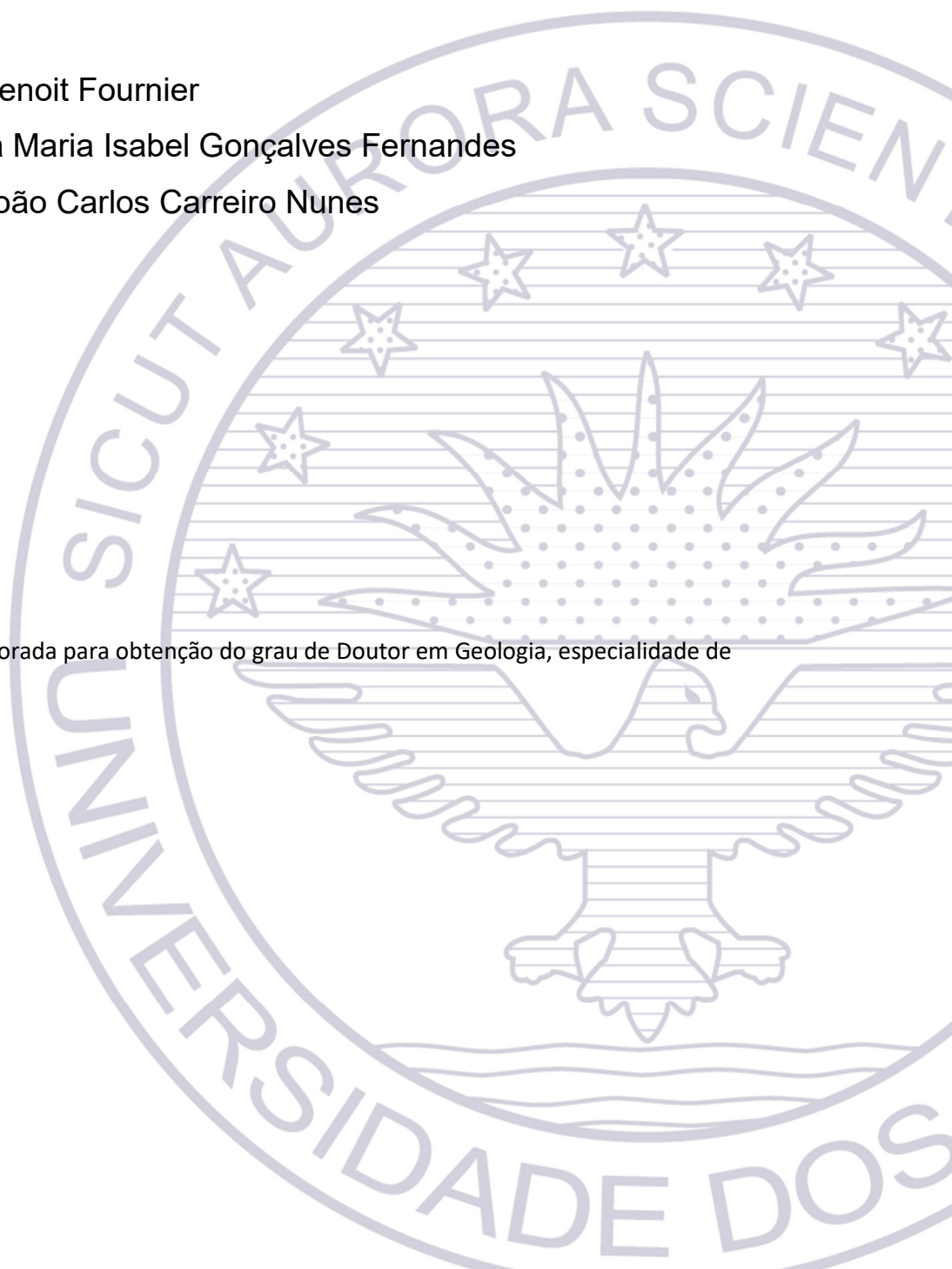
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**À Isabel, ao Jorge e à Teresa pela imensa
paciência e pelo apoio incondicional
Aos meus pais e irmãs pelo constante
apoio e incentivo mesmo à distância**

*“(...) mãe tem o jeito das flores
Que nascem onde ninguém espera
Desabrocha cheia de cores
Quando o mundo precisa da primavera (...)”*

"Jeito das Flores" de Sandra Fernandes

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Abstract

Concrete is one of the most used building materials worldwide but over the years it has been noticed that its durability and resistance have been affected by different types of pathologies. One of these types is known as the alkali-silica reaction (ASR) which is a chemical reaction that occurs between reactive minerals in the aggregates and the alkalis in the cement paste.

Volcanic rocks are present in different geological environments and are used like other types of rocks as concrete aggregates mostly because of their local availability. Their potential alkali-silica reactivity is well known for some andesites and rhyolites. However, some uncertainties remain for basalts even now and there is no consensus among the scientific community about their deleterious character. Deleterious and non-deleterious results were obtained by different researchers when basaltic aggregates were tested using different methods in the laboratory. This inconsistent information can indeed be obtained, especially when the accelerated mortar bar test (AMBT) is used to evaluate their potential alkali reactivity. To better understand this inconsistency and the role of basalts in the ASR, several volcanic aggregates from different locations (i.e. Azores, Brazil, Canada, Canary and Hawaiian Islands, Iceland, Japan, Mozambique, New Zealand, Norway, Turkey) were selected for the present work. The majority of the aggregates are of basic composition. Andesites and rhyolites were also included for comparative purposes due to their known deleterious character.

A set of methods were used to characterize the potential alkali-reactivity of all the aggregates. These included the petrographic method, accelerated mortar bar (AMBT) and concrete prism tests (CPT), damage rating index (DRI method) and gel pat test (GPT). The main results obtained showed that: (1) volcanic glass is present in several aggregate samples, with SiO₂ content ranging from 44% to 80%; (2) a part of the aggregates are considered reactive in the AMBT method; (3) only some samples of volcanic origin were considered reactive in the CPT, among them are included the ones containing volcanic sand fractions, one mixed-gravel and two andesite coarse aggregates; (4) the highest DRI numbers are mainly related to the aggregate samples with volcanic sand fractions, and (5) the presence of secondary deposits of gel in several sand particles in the GPT is correlated with the highest DRI numbers; (5) the andesites from Japan and Turkey are considered reactive but not the rhyolite from Mozambique.

Keywords: basalts, volcanic aggregates, volcanic glass, alkali-silica reaction, islands, petrographic characterization, accelerated expansion test, concrete prism test, DRI, GPT.

Resumo

O betão é um dos materiais de construção mais utilizados em todo o mundo, mas ao longo dos anos a sua durabilidade e resistência têm sido afetadas por diversos tipos de patologias. Uma dessas patologias é conhecida como reação álcalis-sílica, (RAS) que é uma reação química que ocorre entre os minerais reativos nos agregados e os álcalis na pasta de cimento.

As rochas vulcânicas presentes em diferentes ambientes geológicos são usadas como agregados para o betão, tal como outros tipos de rocha, principalmente devido à sua disponibilidade local. A reatividade potencial aos álcalis é bem conhecida em alguns andesitos e riólitos. No entanto em relação aos basaltos, estes ainda permanecem com algumas incertezas não existindo ainda consenso entre a comunidade científica sobre seu caráter deletério. Diferentes investigações identificaram alguns basaltos como reativos quando submetidos a ensaios laboratoriais de expansão enquanto que outros foram considerados não reativos pelos mesmos métodos. Esta ambiguidade de resultados é obtida, especialmente quando é usado o método acelerado da barra de argamassa (AMBT) para avaliar a reatividade dos agregados. De modo a compreender melhor estes resultados e o papel dos basaltos relativamente à RAS, vários agregados vulcânicos de diferentes lugares (ou seja, Açores, Brasil, Canadá, Ilhas Canárias e Havaianas, Islândia, Japão, Moçambique, Nova Zelândia, Noruega, Turquia) foram selecionados para o presente trabalho. A maioria dos agregados são de composição básica, no entanto, para fins comparativos também foram incluídos neste trabalho andesitos e riólitos cuja reatividade é conhecida na literatura.

Um conjunto de métodos foi usado para caracterizar a reatividade dos agregados: o método petrográfico, o método acelerado da barra de argamassa (AMBT), o método de prisma de betão (CPT), o *damage rating index* (DRI) e o *gel pat test* (GPT). Os principais resultados obtidos mostraram que: (1) o método petrográfico identificou a presença de vidro vulcânico em vários agregados com composição em SiO₂ entre 44% e 80%; (2) uma parte dos agregados são considerados reativos pelo método AMBT; (3) apenas alguns agregados foram considerados reativos pelo método CPT, entre os quais destacam-se as misturas que incluem frações de areia vulcânica; (4) os maiores valores de DRI estão principalmente relacionados com os agregados que contêm areia vulcânica como agregado fino e (5) a presença de gel em várias partículas de areia identificadas no método de GPT estão correlacionados com os valores mais elevados obtidos no ensaio DRI; (5) os dois andesitos estudados são considerados reativos, mas o riólito de Moçambique é classificado como não reativo.

Palavras-chave: basaltos, agregados vulcânicos, vidro vulcânico, reação álcalis-sílica, ilhas, caracterização petrográfica, método acelerado da barra de argamassa, o método de prisma de betão, DRI, GPT.

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Contents

Abstract	iii
Resumo	iv
Acknowledgements	v
Contents	vii
List of acronyms and abbreviations	xii
List of Figures	xiv
List of tables	xxvii
Chapter 1. Introduction	1
1.1. Scope of the work	2
1.2. Objectives	4
1.3. Organization of the thesis	5
Chapter 2. Deterioration of concrete by alkali-silica reaction	7
2.1. The definition of alkali-aggregate reaction	8
2.2. History of ASR	8
2.3. Occurrence	14
2.3.1. Reactive forms of silica	17
2.3.2. Presence of alkalis in concrete	22
2.3.3. Moisture	26
2.4. Diagnosis	28
2.4.1. Visual symptoms of ASR	29
2.4.2. Laboratory investigations	37
2.5. Preventive measures	39
2.5.1. Limiting moisture	39
2.5.2. The use of non-reactive aggregates	41
2.5.3. Minimize the alkali content of the pore solution	44
2.5.4. Supplementary cement materials (SMCs)	44
2.5.5. Lithium-based compounds	58
Chapter 3. Alkali-silica reaction in volcanic aggregates	60
3.1. Case studies	61
3.1.1. Concrete structures made with volcanic aggregates	62

3.1.2. Volcanic aggregates considered potentially reactive by different test methods	82
3.2. Petrography of volcanic rocks and ASR	110
3.2.1. Petrography of volcanic rocks at different tectonic settings	111
3.2.2. Deleterious constituents of volcanic rocks	116
Chapter 4. Materials and Methods	124
4.1. Materials	125
4.2. Methods	128
4.2.1. Aggregates	130
Petrographic examination	130
Complementary techniques to petrography	134
Scanning electron microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)	135
Electron Microprobe analysis (EPMA)	137
Chemical analysis of the whole-rock composition	138
4.2.2. Mortar	141
Accelerated mortar-bar test at 80°C	141
4.2.3. Concrete	144
Concrete prism test at 38°C	144
Gel Pat Test	147
Petrographic examination	150
Damage Rating Index (DRI method)	150
Petrographic examination of mortar and hardened concrete	156
4.2.4. Methods used in the present work	161
Chapter 5. Results	164
5.1. Sites/samples from Islands	166
5.1.1. Geological setting	166
Azores Archipelago (Portugal)	166
Canary Islands (Spain)	167
Hawaiian Islands (USA)	169
Iceland	170
Japan	172
New Zealand	174
5.1.2. Characterization of volcanic aggregates from Islands	176
5.1.2.1. Geochemical analysis, TAS diagram and CIPW norm	176
5.1.2.2. Petrographic examination	181

Azores Archipelago (Portugal)	181
Canary Islands (Spain)	184
Hawaiian Islands (USA)	189
Iceland	200
Japan	222
New Zealand	224
5.13. Mortar studies	235
5.1.3.1. Expansion tests - Accelerated mortar-bar test at 80°C (CSA A23.2-25A/ASTM C 1260)	235
Azores Archipelago (Portugal)	235
Canary Islands (Spain)	237
Hawaiian Islands (USA)	237
Iceland	238
Japan	240
New Zealand	241
5.1.3.2. Post-mortem mortar petrography	242
Azores Archipelago (Portugal)	242
Canary Islands (Spain)	244
Hawaiian Islands (USA)	245
Iceland	247
Japan	253
New Zealand	254
5.1.4. Concrete studies	256
5.1.4.1. Expansion tests - Concrete prism test at 38°C (CSA A23.2-14A, 2015)	256
Azores Archipelago (Portugal)	256
Canary Islands (Spain)	258
Hawaiian Islands (USA)	258
Iceland	259
Japan	261
New Zealand	262
5.1.4.2. Gel Pat test	262
5.1.4.3. Petrographic examination - Damage Rating Index (DRI)	267
5.1.4.4. Post-mortem concrete petrography	272
Azores Archipelago (Portugal)	272

Canary Islands (Spain)	274
Hawaiian Islands (USA)	275
Iceland	277
Japan	280
New Zealand	281
5.2. Sites/samples from Continental Regions	283
5.2.1. Geological setting	283
Brazil	283
Canada	284
Mozambique	286
Norway	287
Turkey	289
5.2.2. Characterization of volcanic aggregates from continental regions	291
5.2.2.1. Geochemical analysis, TAS diagram and CIPW norm	291
5.2.2.2. Petrographic examination	293
Brazil	293
Canada	299
Mozambique	303
Norway	304
Turkey	308
5.2.3. Mortar studies	314
5.2.3.1. Expansion tests - Accelerated mortar-bar test at 80°C (CSA A23.2-25A/ASTM C 1260)	314
Brazil	315
Canada	315
Mozambique	316
Norway	317
Turkey	318
5.1.3.2. Post-mortem mortar petrography	319
Brazil	319
Canada	321
Mozambique	322
Norway	324
Turkey	325

5.2.4. Concrete studies	326
5.2.4.1. Expansion tests - Concrete prism test at 38°C (CSA A23.2-14A, 2015)	326
Brazil	326
Canada	327
Mozambique	328
Norway	329
Turkey	330
Spratt (Canada)	331
5.2.4.2. Gel Pat test	332
5.2.4.3. Petrographic examination - Damage Rating Index (DRI)	335
5.2.4.4. Post-mortem concrete petrography	339
Brazil	339
<i>Spratt</i> (from Canada)	340
Mozambique	341
Turkey	342
Chapter 6. Analysis and discussion	344
6.1. Petrography of the aggregates, rock suites and geological setting	347
6.2. Correlation between the results of laboratory investigations	354
6.3. Post mortem petrography and gel formation	358
Chapter 7. Conclusions and future research	361
7.1. Conclusions	362
7.2. Future research	367
References	368

List of acronyms and abbreviations

AAR	Alkali-Aggregate Reaction
ABNT	Brazilian Association of Technical Standards
ABCP	Brazilian Portland Cement Association
ABS	Air-cooled blast furnace slag
ACI	American Concrete Institute
ACPT	Accelerated Concrete Prism Test
ACR	Alkali-Carbonate Reaction
ACTLABS	Activation Laboratories
AMBT	Accelerated Mortar Bar Test
ASR	Alkali-Silica Reaction
ASTM	American Society for Testing and Materials
BCA	British Cement Association
BFS	Blast furnace slag
BS	British Standards
BSE	Backscattered electron
CC	Calcined clays
CCANZ	Cement and Concrete Association of New Zealand
CESP	Producer of electricity in the state of São Paulo
CIPW	Cross-Iddings-Pirsson-Washington
CPT	Concrete Prism Test
CSA	Canadian Standards Association
C/S	Layered chlorite and smectite
DEF	Delayed Ettringite Formation
DRI	Damaging Rating Index
EDS	Energy-Dispersive X-Ray Spectrometer
EL	Elevation
EPMA	Electron-Probe Micro-Analyser
FA	Fly ash
GGBS	Ground granulated blast furnace slag
GPT	Gel Pat Test
HP	High-purity limestone coarse aggregate
IBRI	Icelandic Building Research Institute
ICAAR	International conference on alkali-aggregate reaction in concrete

IRAM	Argentine Institute of Standardization and Certification
JIS	Japanese standards
LNEC	Laboratório Nacional de Engenharia Civil
LOI	Loss On Ignition
MK	Metakaolin
NBR	Brazilian Association of Technical standards
NBRI	National Building Research Institute
Na ₂ O _{eq}	Equivalent sodium oxide
NP	Portuguese Standard
OPC	Ordinary Portland Cement
OSIPOV	Test method proposed by Dr Osipov where fragments of aggregate are exposed to a temperature of 1000°C for 1 min
PPL	Plane Polarized Light
RCS	Reinforced concrete structures
ReAVA project	Characterization of potential reactivity of the volcanic aggregates from the Azores Archipelago: implications on the durability of concrete structures
RH	Relative Humidity
RHA	Rice husk ash
RILEM	Réunion Internationale des Laboratoires et Experts des Matériaux
SCMs	Supplementary Cementitious Materials
SEM	Scanning Electron Microscopy
SF	Silica fume or microsilica
s.l.	“sensu lato”
SRC	Steel Reinforced Concrete
s.s.	“sensu stricto”
TAS	Total Alkali-Silica
TC	Technical Committees
USA	United States of America
UK	United Kingdom
w/c	Water to cement ratio
Wr/sp	Admixture with Water reducer/ superplasticizers
Wt%	Weight per cent
XPL	Cross-Polarized Light

List of Figures

Figure 2.1. Thomas Stanton standing beside a Bridge Parapet Wall with signs of ASR (Thomas et al., 2013b)	9
Figure 2.2. Simplified process of ASR based on the work of Deschenes et al (2009): A) alkali hydroxide ions reacting with reactive aggregates, B) expansive gel formed and C) cracking of the aggregate and cement paste.	15
Figure 2.3. Differences in the crystalline structure of opal and quartz (Dent Glasser and Kataoka, 1981).	20
Figure 2.4. Pessimism behaviour; w/c=0.4 and a/c= 2.75 ratios, alkali content 6 kg/m ³ (Hobbs, 1988).	21
Figure 2.5. The effect of relative humidity on the expansion of concrete due to ASR (Poole, 1992).	27
Figure 2.6. Schematic representation of ASR cracking: (A) map-cracking (ACI 1998) and (B) in one or two directions in RCS (Figueira et al., 2019).	30
Figure 2.7. Patterns of cracking in concrete due to ASR: (A) map-cracking in concrete pavement, (B) Map cracking in the wing wall of a highway bridge structure, and (C) longitudinal cracking following the main reinforcement in columns of a highway concrete structure (with compliments of B. Fournier).	31
Figure 2.8. Misalignment in the crest of a concrete dam due to ASR (Fernandes and Broekmans 2013).	33
Figure 2.9. Interior wall in two different dams: (A) efflorescence and (B) gel exudation (Fernandes and Broekmans 2013).	34
Figure 2.10. Example of pop-out in a concrete element (Ramos, 2013).	34
Figure 2.11. Internal cracking pattern caused by ASR: (A) reactive silica in the sand fraction and (B) reactive silica in the coarse aggregate (BCA, 1992).	38
Figure 2.12. Expansion evolution of accelerated mortar bar tests performed on samples prepared with various slag replacement levels (Hooton et al., 2000).	49
Figure 2.13. Effect of ash composition (Type F fly ash: FM; Type CI fly ash: BD, SD I, WM; Type CH fly ash: EW, OK) and of replacement level on expansion due to ASR. (Shehata and Thomas 2000).	51
Figure 2.14. Expansion evolution of mortar bars containing different levels of highly reactive metakaolin (HRM) as cement replacement: a) with Spratt aggregate and b) with Sudbury aggregate (Ramlochan et al 2000).	52
Figure 2.15. Expansion evolution of concrete prisms containing different levels of highly reactive metakaolin (HRM) as cement replacement: A) Sudbury aggregate, B) Spratt aggregate (Ramlochan et al., 2000).	53
Figure 2.16. Expansion evolution of mortar bars containing Ordinary Portland Cement with microsilica (MS) and natural pozzolan (R) both at different replacement values (Ásgeirsson, 1986).	55
Figure 2.17. Expansion of concrete prisms containing: A) 4, B) 8 and C) 12% SF as replacement of the OPC (Ordinary Portland cement). The different types of SF used are as follows: SF from Canada: UND – Undensified, PEL-Pelletized, DEN1 - Densified #1; SF from the USA: DEN2 - Densified #2, SLU – Slurried).	56
Figure 2.18. Schematic mechanism of ASR when Li is present (Feng et al., 2010).	59

Figure 4.1. Map view of the origin of the selected aggregate samples: Azores (all islands); Brazil (Ilha Solteira); Canada (near Québec city); Canary Islands (Tenerife and El Hierro Islands); Iceland (Western and Southeastern areas); Japan (Western Hokkaido); Mozambique (Karoo area); New Zealand (North and South Islands); Norway (Near Oslo); Turkey (near Aliağa).	125
Figure 4.2. Integrated assessment scheme for the potential AAR (RILEM AAR-0, 2016).	129
Figure 4.3. Swot analysis for the petrographic examination method.	134
Figure 4.4. Different sputter coater equipment was used for carbon coating the samples (A and B) and (C) sample holders.	136
Figure 4.5. Scanning electron microscope	136
Figure 4.6. Example of an EDS spectrum.	137
Figure 4.7. Electron microprobe analysis (EPMA)	138
Figure 4.8. TAS diagram (Le Bas et al., 1986).	139
Figure 4.9. SWOT analysis of AMBT method.	142
Figure 4.10. Measuring the mortar bar of the AMBT method.	143
Figure 4.11. SWOT analysis of CPT method.	145
Figure 4.12. Measurement of a prism for the CPT method.	147
Figure 4.13. Plastic container /pails: (a) with a wick and 3 prims inside a rack; (b) inside a chamber at 38°C.	147
Figure 4.14. SWOT analysis of GPT method.	149
Figure 4.15. Example of a concrete prism subject to GPT method.	150
Figure 4.16. Concrete polished surface with a drawn grid of 1 cm ² .	152
Figure 4.17. Example of a DRI damage map in an excel sheet.	153
Figure 4.18. SWOT analysis of DRI method.	155
Figure 4.19. Schematic diagram with different stages of the complexity of petrographic investigation (Poole and Sims, 2016).	159
Figure 5.1. General geotectonic setting of Azores Archipelago (Nunes, 2014)	167
Figure 5.2. The Canary (red) and Madeira (blue) Volcanic Provinces. Thick dashed lines mark centres of possible hotspot tracks (@ Hoernle and Carracedo, 2009).	168
Figure 5.3. Geotectonic setting of Hawaiian Islands. (@ Walker, 1990).	170
Figure 5.4. Geotectonic setting of Iceland. (@ Thordarson and Höskuldsson, 2014). RR: Reykjanes Ridge; RVB: Reykjanes Volcanic Belt; WVZ: West Volcanic Zone; MIB: Mid-Iceland Belt; EVZ: East Volcanic Zone; NVZ: North Volcanic Zone; TZF: Tjörnes Fracture Zone; KR: Kolbeinsey Ridge; ÖVB: Öräli Volcanic Belt and SVB: Snæfellsnes Volcanic Belt.	171
Figure 5.5. Geotectonic setting of Japan. Yellow star: Boso triple junction. Light blue lines, major inland faults (Van Horne et al., 2017). MTL: Median Tectonic Line; ISTL: Itoigawa-Shizuoka Tectonic Line; TTL: Tanakura Tectonic Line; Ka: Kanto Mountains; De: Dewa Hills; Ou: Ou Backbone Range.	174
Figure 5.6. Tectonic setting of New Zealand. (Wallace et al., 2004).	175

Figure 5.7. TAS diagram (after Le Bas et al 1986) of the volcanic aggregates from different islands: 1- Azores Archipelago (Portugal), 2- Canary Islands (Spain), 3-Iceland, 4- Japan, 5-New Zealand and 6- Hawaiian Islands (USA).	179
Figure 5.8. AFM diagram (after Irvine and Baragar, 1971) of the volcanic aggregates studied where most of the rocks follow a tholeiitic trend. Iceland (green), Japan (blue), New Zealand (light blue) and the Hawaiian Islands (pink). A = Na ₂ O + K ₂ O; F = FeO + 0.8998 Fe ₂ O ₃ ; M = MgO (wt%).	180
Figure 5.9. Block samples of the Azorean rocks were used as aggregates. Only the CRV sample is formed by crushed aggregate.	182
Figure 5.10. Photomicrographs of Azorean aggregates. Photo A, B, D and E in XPL; C and F in PPL. A) Basalt with pilotassitic groundmass (TER-SM1); B) Calcite filling a crack (SMA-SM1); C) Iddingsite rims in olivine crystals (SMA-SM2); D) Analcime filling a vesicle (SMA-SM1); E) Anorthoclase crystals in the trachyte sample (TER-SM1), and F) Interstitial volcanic glass (SMG-SM1).	183
Figure 5.11. Canary samples of aggregate in crushed rock, are split into different fractions according to the texture and colour.	184
Figure 5.12. Photomicrographs of sample CANY1. All photos are in PPL. A) Subaphyric texture; B) and C) Phenocryst of clinopyroxene; D) Presence of zeolite; E) Interstitial volcanic glass (brownish, amorphous); F) biotite.	185
Figure 5.13. Sample CANY1. Yellowish material and and location of the EPMA analyses..	186
Figure 5.14. Sample CANY1. Volcanic glass and respective examination points.	187
Figure 5.15. Photomicrographs of sample CANY2: A, B and D in XPL, C in PPL A) Vesicular and porphyritic texture; B) Skeletal olivine; C) Plagioclase with peculiar sieve-like texture; D) Vesicles filled with carbonate minerals.	188
Figure 5.16. Sample CANY2. Photomicrograph (A) and BSE image (B) and respective EDS spectra of zeolite partly filling a void (E180 and E181).	189
Figure 5.17. Macroscopic photos of the different aggregates and facies from Hawaiian aggregates.	190
Figure 5.18. Photomicrographs of Hawaiian samples. Photos B, C, D and F in XPL. Photos A and F in PPL. A) Variolitic texture (HW5); B) Embayed olivine (HW1); C) Skeletal olivine rimmed by iddingsite (HW5); D) Olivine with peculiar textures (HW1); E) Orthopyroxene (HW6) and F) Glomeroporphyritic clusters of olivine (HW2).	192
Figure 5.19. Photomicrographs of brownish volcanic glass in the Hawaiian samples. The red arrows point to the interstitial brownish volcanic glass and the red circles to the vesicular glass. All photos are in PPL. A) Interstitial volcanic glass in HW1 sample; B) Interstitial volcanic glass in HW3 C) Vesicular glass containing minute crystals of iron ore and needles of apatite in HW3; D) Vesicular glass containing minute particles of iron ore and needles of apatite in HW5; E) Vesicular glass containing minute particles of iron ore and needles of apatite in HW6; F) Interstitial volcanic glass in HW7.	193
Figure 5.20. Sample HW1. Brownish volcanic glass and respective examination points.	194
Figure 5.21. Sample HW3. Microphotograph (A) and BSE image (B) and respective points of analysis.	195
Figure 5.22. Sample HW5. Interstitial brownish volcanic glass and respective examination points for the composition of the volcanic glass.	196
Figure 5.23. Sample HW6. Microphotograph (A), BSE image (B) and points of analysis of interstitial volcanic glass.	197

Figure 5.24. Sample HW7. Microphotograph (A), BSE images (B1 and B2) and respective points of analysis. Image B2 corresponds to an amplification of the area in the red circle	198
Figure 5.25. Sample HW7. Microphotograph (A), BSE image (B) and respective points of analysis.	199
Figure 5.26. Icelandic aggregates are divided into fractions based on the texture and the colour of the particles.	200
Figure 5.27. Photomicrographs of ICL1 sample: C, D and E in XPL; A, B and F in PPL. A) Variolitic texture; B) Basalt containing altered volcanic glass; C) Pore space with zeolite and chlorite/smectite in a metabasalt; D) Tridymite in rhyolite aggregate particle; E) Dacite with spherulitic texture involving an euhedral crystal of quartz; F) Volcanic glass with brown spherical bodies and pores.	203
Figure 5.28. Basalt in ICL1-F1 (basalt). Photomicrograph (A), BSE image (B) and respective EDS spectra of volcanic glass (E44 and E46).	204
Figure 5.29. Metabasalt in ICL1-F1. Photomicrograph (A) and BSE image (B) and respective points of analysis.	205
Figure 5.30A. Dacite in ICL1-F2: Photomicrograph (A) and BSE image (B) and respective points of analysis.	206
Figure 5.30B. Dacite in ICL1-F2: EDS spectra of quartz (E20 and E22) and plagioclase (E23), in Figure 5.30A.	207
Figure 5.30C. Sample ICL1-F2 (Dacite). Microphotograph (A) and BSE image (B) (a detail of Figure 5.30A) with the points of analysis.	208
Figure 5.31. Rhyolite in ICL1-F3: A) Image with the points of analysis 1 to 5 and B) Image with the points of analysis 6 to 8.	209
Figure 5.32A. Metabasalt in ICL1-F4: Photomicrographs (A) and BSE image (B) indicating the points of analysis.	210
Figure 5.32B. Metabasalt in ICL1-F4: EDS spectra of zeolites (E57 and E58).	210
Figure 5.33. Photomicrographs of ICL2 sample: A, B, E and F in XPL; C and D in PPL. The red arrows point to the devitrified glass material in A) and chlorite in B). A) Basalt with subophitic texture and scattered devitrified glass; B) Basalt with subophitic texture and scattered chlorite; C) Large euhedral olivine phenocryst in basalt; D) Basalt with a peculiar texture containing fans of dendritic clinopyroxene; E) Metabasalt with cracked plagioclase and a vesicle filled with zeolite, in the nucleus, and chlorite at the rim; F) Rhyolite aggregate particle.	212
Figure 5.34A. Sample ICL2-F1 (metabasalt). Photomicrographs (A) and BSE images (B) and respective points of analysis.	213
Figure 5.34B. EDS spectra of volcanic glass (E47 and E48).	213
Figure 5.35. Sample ICL2-F2 (Basalt). Photomicrographs (A) and BSE images (B) and respective points of analysis..	214
Figure 5.36. Photomicrographs of ICL3 sample: A, B, E and F in XPL; C and D in PPL. A) Plagioclase phenocryst; B) Basalt with subophitic texture; C) Basalt with variolitic texture; D) Vesicular texture; E) Glomeroporphyritic clusters of plagioclase; F) Skeletal crystal of olivine.	215
Figure 5.37. Photomicrographs of ICL4 sample: B in XPL; A, C, D, E and F in PPL. A) Banded lava; B) Tachylite groundmass in a Basalt particle; C) Feathery clinopyroxene in a basaltic particle; D) Glassy basalt; E) Prismatic plagioclase lath and pyrite crystal; F) Altered	217

p Photomicrographs of ICL4 sample: B in XPL; A, C, D, E and F in PPL. A) Banded lava; B) Tachylite groundmass in a Basalt particle; C) Feathery clinopyroxene in a basaltic particle; D) Glassy basalt; E) Prismatic plagioclase lath and pyrite crystal; F) Altered plagioclase in a coarse-grained particle (similar to gabbro).plagioclase in a coarse-grained particle (similar to gabbro).	
Figure 5.38. Hydrothermal rock in ICL4-F3. Photomicrographs (A) and BSE images (B) show the locations of the points of analysis. EDS spectrum of pyrite (E73).	218
Figure 5.39. Basalt in ICL4-F3. Photomicrographs (A) and BSE images (B) with respective points of analysis.	219
Figure 5.40. Glassy basalt in ICL4-F4. Photomicrographs (A) and BSE images (B)with respective points of analysis (1-6).	220
Figure 5.41. Glassy basalt in ICL4-F4. Photomicrographs (A) and BSE images (B) showing the points of analysis (1-5).	221
Figure 5.42. Macroscopic photos of JAP aggregates: A) general view and B) detailed perspective.	222
Figure 5.43. Photomicrographs of JAP andesite: A, C and D in XPL, B in PPL. A) Porphyritic texture; B) Amphibole (hornblende); C) Zoned plagioclase crystal with sieve texture; D) Section of the groundmass with tridymite.	223
Figure 5.44A. Sample JAP (Andesite). BSE image and respective points of analysis.	223
Figure 5.44B. Sample JAP (Andesite). EDS spectra of alkaline feldspar (E42), plagioclase (E43) and a silica mineral which might be tridymite (E44).	224
Figure 5.45. Macroscopic photos of the different aggregates and facies from New Zealand.	225
Figure 5.46. Photomicrographs of NZ1 sample: B, C and D in XPL, A, E and F in PPL. A) Porphyritic texture with brownish interstitial volcanic glass; B) Iddingsitized olivine with fractures filled with saponite; C) Vesicle filled with zeolite and carbonate; D) Vesicle filled with chlorite and clay minerals; E) Chlorite and smectite in the interstices of the rock; F) Volcanic glass (palagonite).	226
Figure 5.47A. Basanite NZ1. Microphotograph (A) and BSE image (B) and respective points of analysis.	227
Figure 5.47B. EDS spectra of zeolite (E117 and E121) and calcite (E119).	228
Figure 5.48. Basanite in NZ1. Photomicrograph (A) , BSE image (B) and respective points of analysis.	229
Figure 5.49. Photomicrographs of NZ2 sample. All photos are in XPL. A) Porphyritic texture; B) Glomeroporphyritic clots of plagioclase; C) Glomeroporphyritic clots of plagioclase and olivine; D) Clinopyroxene.	230
Figure 5.50. Photomicrographs of NZ3 sample: A and B in XPL; C and D in PPL. A) Porphyritic texture and subophitic textures in a coarser matrix; B) Porphyritic texture in a fine-grained matrix; C) Tachylite in a vesicular aggregate particular; D) Interstitial volcanic glass indicated by red arrows.	231
Figure 5.51. Basalt of NZ3. Photomicrograph (A) and BSE image (B) and respective points of analysis (1-3).	232
Figure 5.52. Basalt in NZ3. Photomicrograph (A) and BSE image (B) and points of analysis of volcanic glass (1-4).	233
Figure 5.53. Basalt in NZ3. Photomicrograph (A) and BSE image (B) and respective points of analysis (1-4).	234

Figure 5.54. Expansion results of the accelerated mortar-bar test at 80°C concerning the Azorean aggregates: thirteen aggregates according to ASTM C 1260 and CRV aggregate according to CSA A23.2-25A.	236
Figure 5.55. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Canary aggregates (CANY1 and CANY2).	237
Figure 5.56. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Hawaiian aggregates.	238
Figure 5.57. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Icelandic aggregates.	239
Figure 5.58. Expansion results of the accelerated mortar-bar method test at 80°C (CSA A23.2-25A) concerning the Japan aggregate.	240
Figure 5.59. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the New Zealand aggregates.	241
Figure 5.60. Photomicrographs of mortar bars incorporating aggregates from the Azores: C in XPL, A, B D, E and F in PPL. A) Volcanic glass in an aggregate particle (FLO-SM1); B) Vitrophyric (glassy) basalt particle (SMG-SM1); C) Shell in the sand fraction (GRA-SM1); D) Crack inside an aggregate particle (SMA-SM2) containing volcanic glass; E) Crack with gel (TER-SM1); F) Pore partly filled with gel (TER-SM1).	243
Figure 5.61. Photomicrographs of mortar bars incorporating aggregates from the Canary Islands. Photo D in XPL. Photos A, B and C in PPL. A) Volcanic glass in an aggregate particle (CANY2); B) Glassy basalt particle (CANY1); C) Pore filled with isotropic brownish material (CANY1).	244
Figure 5.62. Photomicrographs of mortar bars incorporating Hawaiian aggregates. All Photos are in PPL. A) Crack with brownish gel crossing two aggregate particles and one pore (HW1); B) Crack with brownish gel crossing two aggregate particles and the cement paste (HW3); C) Crack with brownish gel crossing one particle and partially surrounding other two particles (HW5/6); D) Crack with brownish gel crossing one particle and surrounding other two particles (HW7); E) Gel inside an aggregate particle and lining it (HW5/6); F) Crack starting in an aggregate particle, filled with brownish gel, and extending into the cement paste (HW5/6).	246
Figure 5.63. Photomicrographs of mortar bars made with ICL1 coarse sand. All Photos are in PPL. A) Crack outlining an aggregate particle with brownish gel; B) Crack within the basaltic aggregate particle; C) Crack within a microcrystalline quartz particle; D) Volcanic glass in a basaltic aggregate particle; E) Detail of the volcanic glass inside a basaltic aggregate particle; F) Air void partly filled with brownish material.	248
Figure 5.64. Photomicrographs of mortar bar incorporating ICL1 fine sand. All Photos are in PPL. . A) Crack with brownish gel associated with the volcanic glass within the basaltic aggregate particle and extending into the cement matrix; B) Crack with brownish gel both in a basaltic aggregate particle and in the cement matrix; C) Crack with brownish gel both in a glassy basalt particle and in the cement matrix; D) Crack with brownish gel crossing a rhyolite particle and the cement matrix; E) Gel within a basaltic aggregate particle; F) basaltic aggregate particle containing cracks with dull, dark brownish gel.	249
Figure 5.65. Photomicrographs of mortar bars made with ICL1 and ICL2 aggregates. All Photos are in PPL. A) Crack with brownish gel within the basalt particle (ICL1); B) Crack with brownish gel within a rhyolitic aggregate particle (ICL1); C) Crack with brownish gel crossing a rhyolite particle and the cement matrix (ICL1); D) Crack with brownish gel in a	250

dark basaltic particle and in the cement matrix (ICL1); E) Gel within a basaltic aggregate particle (ICL2); F) Void filled with brownish material (ICL2).	
Figure 5.66. Photomicrographs of mortar bars incorporating ICL3 sand and ICL4 aggregate. All Photos are in PPL. A) Empty crack at the edge of the thin section caused by the thin section preparation (ICL3 sand); B) Brownish gel in a crack within a dark basaltic particle that extends into the cement paste (ICL4); C) Brownish gel in cracks inside a rhyolite particle that extends into the cement paste (ICL4); D) Void with ettringite and lined by gel (ICL4).	251
Figure 5.67. Photomicrographs of mortar bar incorporating ICL4 sand and GBS sand. All Photos are in PPL. A) Large cracks in the cement paste (ICL4 sand); B) Brownish gel lining an aggregate particle (ICL4 sand); C) Brownish gel within a basalt particle that extends into the cement paste (GBS sand); D) Brownish gel in a crack within a rhyolitic particle and that extends into the cement paste (GBS sand).	252
Figure 5.68. Photomicrographs of mortar bar incorporating JAP aggregate. All photos are in PPL. A) Crack crossing aggregate particles and the cement paste, filled with an isotropic brownish material; B) Brownish material restricted to a crack inside an aggregate particle; C) Huge empty crack in an aggregate particle; D) Pore partly filled by brownish material and rimmed by colourless gel.	253
Figure 5.68 (continued). Photomicrographs of mortar bar incorporating JAP aggregate. All photos are in PPL. E) Pore partly lined with gel and needle crystals of ettringite; F) Pore partly filled with gel and crystals of ettringite.	254
Figure 5.69. Photomicrographs of mortar bars incorporating New Zealand aggregates: B in XPL; A, C, D, E and F in PPL. A) Volcanic glass in two aggregate particles with different shades of brown colour (NZ1); B) Plagioclase crystal particle in the finer fraction of the aggregates (NZ2); C) Glassy basaltic particle (NZ3); D) Aggregate particle cut by a crack filled with a yellow material (NZ1).	255
Figure 5.69 (continued). Photomicrographs of mortar bars incorporating New Zealand aggregates: All in PPL. E) Crack crossing an aggregate particle filled with isotropic brownish gel (NZ3); F) Yellowish gel restricted to a crack inside an aggregate particle (NZ3).	256
Figure 5.70. Expansion results of the CPT method test at 38°C concerning the Azorean aggregates (RILEM AAR-3; CSA A23.2-14A).	257
Figure 5.71. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2019) concerning the Canary aggregates.	258
Figure 5.72. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2019) concerning the Canary aggregates.	259
Figure 5.73. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the Icelandic aggregates.	260
Figure 5.74. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2019) concerning the Japanese aggregates.	261
Figure 5.75. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2019) concerning the New Zealand aggregates.	262
Figure 5.76. Photographs of the results of the GPT were used in different concrete sections at week 19. A) concrete section with CRV aggregate; B) Detail of the concrete (CRV) showing deposits of gel on an aggregate particle; C) Concrete section with CANY2 aggregate; D) Detail of the concrete (CANY2); E) Concrete section with CANY1 aggregate; F) Detail of the concrete (CANY1) with one deposit of gel on an aggregate particle.	264
Figure 5.77. Photographs of the results of the GPT were used in different concrete sections at week 19. A) Concrete section with HW7 sand aggregate; B) Detail of the concrete section	265

(HW7 sand) showing deposits of gel on sand particles; C) Concrete section with ICL1 coarse sand aggregate; D) Detail of the concrete section (ICL1 coarse sand) showing deposits of gel on sand particles; E) Concrete section with ICL1 fine sand aggregate and F) Detail of the concrete section (ICL1 fine sand) showing deposits of gel on sand particle and white film of gel covering the section.

Figure 5.78. Photographs of the results of the GPT were used in different concrete sections at week 19. A) Concrete section with JAP aggregate; B) Detail of the concrete section (JAP) showing numerous deposits of gel on coarse aggregate particles; C) Concrete section with NZ2 aggregate; D) Detail of the concrete section (NZ2) showing deposits of gel on some coarse aggregate particles; E) Concrete section with NZ3 aggregate; F) Detailed of the concrete section (NZ3) showing deposits of gel and white film of gel at the surface of the section. 266

Figure 5.79. Photographs were obtained under a stereo binocular microscope of Azorean concrete prisms. A) Concrete with no cracks in the cement paste and only showing a closed crack in the aggregate particle in the centre of the image (FAI-SM1); B) Concrete with open cracks in the cement paste, closed crack in the aggregate particle and partially debonding of the aggregate particle in the upper part of the image (FLO-SM1). 269

Figure 5.80. Photographs of concrete prisms incorporating New Zealand aggregates. A) Concrete with no cracks in the cement paste and in the aggregate particles (NZ2); B) Concrete with open cracks in an aggregate particle and an air void filled with ASR gel (NZ3). 269

Figure 5.81. Photographs of concrete prism incorporating HW7 sand and HP (non-reactive) coarse aggregate. A) Concrete with several cracks in the cement matrix and crossing different basalt aggregate particles and HP particles, as pointed by the red arrows; B) Concrete with a reacted aggregate particle (red arrows); C) Several cracks in the basalt particles and also in the cement matrix, with gel (red arrows); D) Gel lining an HP particle and a basalt particle with gel, extending into the cement paste and crossing and lining other particles. 270

Figure 5.82. Photographs of concrete prisms incorporating ICL1 coarse and fine sands. A) Concrete with a crack with gel crossing HP particle and lining other HP particle (ICL1 coarse sand); B) Basalt with an open crack partly filled with reaction product, that extends into the cement paste and an HP particle rimmed by gel (red arrows); C) Reactive particle with ASR gel extending into the cement matrix and pore partly filled with gel (ICL1 fine sand) (red arrows); D) Basalt particle with an open crack and gel partially filling cracks in the cement paste (ICL1 fine sand). 271

Figure 5.83. Photographs of concrete prisms incorporating the JAP aggregate. A) Open crack with some gel in an andesite aggregate particle extending into the cement paste; B) Several open cracks in the two andesitic aggregate particles and gel in the cement paste (red arrows). 272

Figure 5.84. Photomicrographs of concrete prisms incorporating Azorean aggregates. All photos are in PPL. A) Crack inside an aggregate particle with a yellowish material (SMA-SM2); B) Gel inside an aggregate particle associated with volcanic glass (SMA-SM1). 273

Figure 5.84. (continued). Photomicrographs of concrete prisms incorporating Azorean aggregates. All photos are in PPL. C) Gel inside an aggregate particle (SMA-SM1); D) Glass inside an aggregate particle (SMA-SM2). 274

Figure 5.85. Photomicrographs of concrete prisms incorporating Canary aggregate (CANY2). All photos are in PPL. A) Zeolites in a vesicle of an aggregate particle; B) Crack connecting different grains of the sand fraction; C) Crack inside an aggregate particle; D) Air void lined by brownish material. 275

Figure 5.86. Photomicrographs of concrete prisms incorporating Hawaiian aggregates. All photos are in PPL. A) Crack in the cement matrix (HW1); B) Crack inside an aggregate 276

- particle (HW4); C) Two air voids lined by brownish material (HW3); D) Crack crossing the cement paste (HW7 CA+FA).
- Figure 5.86. (continued).** Photomicrographs of concrete prisms incorporating Hawaiian aggregates. All photos are in PPL. E) Crack in the cement paste and surrounding the aggregate particle (HW7 CA+FA); F) Crack in the cement paste (HW7 sand). 277
- Figure 5.87.** Photomicrographs of concrete prisms incorporating Icelandic aggregates. All photos are in PPL. A) Crack crossing glassy basalt particle (ICL1 coarse sand); B) Crack crossing a rhyolite particle and the cement paste (ICL1 coarse sand); C) Limestone aggregate particles outlined by brownish material and connecting by a crack with an air void (ICL1 coarse sand); D) Crack in the cement matrix outlining some aggregate particles (ICL1 fine sand). 278
- Figure 5.87 (continued).** Photomicrographs of concrete prisms incorporating Icelandic aggregates. All photos are in PPL. E) Cracks in the limestone aggregate particle (ICL1 fine sand); F) Wide crack crossing a glassy basalt particle (ICL2); G) Crack in the cement matrix (ICL3); H) Crack inside a rhyolite aggregate particle (ICL4); I) Limestone aggregate particle debonded from the cement matrix (ICL4 sand); J) Crack starting in rhyolite aggregate particle and outlining other aggregate particles (ICL4 sand). The red arrows point to the cracks. 280
- Figure 5.88.** Photomicrographs of concrete prism incorporating the JAP aggregate. All photos are in PPL. A) Crack in the cement matrix with brownish gel, also cutting an aggregate particle; B) Crack inside an aggregate particle and in the cement matrix; C) Crack inside an aggregate particle but with no continuity into the cement matrix; D) Crack partly filled with brownish material surrounding the aggregate particle. 281
- Figure 5.89.** Photomicrographs of concrete prisms incorporating New Zealand aggregate. All photos are in PPL. A) Thin crack in the cement matrix (NZ2); B) Crack with brownish material in the cement matrix (NZ2); C) Cracks in the cement matrix, one with brownish material, connecting aggregate particles (NZ3); D) Crack with rare brownish material in the cement matrix (NZ3). 282
- Figure 5.89. (continued).** Photomicrographs of concrete prisms incorporating New Zealand aggregate. All photos are in PPL. E) Air void partly filled with a brownish material; F) Air void partly filled with a brownish material. 280
- Figure 5.90.** Map of the Paraná Continental flood (adapted from Mincato, 2000). The red arrow points to Ilha Solteira. 284
- Figure 5.91.** Map of the Appalachian orogeny in Canada and NE USA. The darker grey colour corresponds to the Humber Zone and light grey colour to the outcrops of the Grenville Province of cratonic Laurentia (Hodych and Cox, 2007). Ma: million of years 285
- Figure 5.92.** Simplified geological map of south-eastern Africa (Miller and Harris, 2006). 287
- Figure 5.93.** Geological map of Bærum Caldroum (Nilsen, 1992). 289
- Figure 5.94.** Geological map of the Bozdivlit andesitic basalts area, Turkey (Fernandes and Andiç-Çakır, 2015). 290
- Figure 5.95.** TAS diagram (after Le Bas et al., 1986) of the volcanic aggregates from continental regions: 1 - Brazil, 2 - Canada, 3 - Mozambique, 4 – Norway and 5 - Turkey. 292
- Figure 5.96.** AFM diagram (after Irvine and Baragar, 1971) of the continental volcanic aggregates studied where BRAZ (Brazil) follows a tholeiitic trend, MOZ (Mozambique) and TK (Turkey) a calc-alkaline trend. A = Na₂O + K₂O; F = FeO + 0.8998 Fe₂O₃; M = MgO (wt.%). 293
- Figure 5.97.** Macroscopic photos of the BRAZ aggregate divided in different fractions. A) General view; B) detail of the fraction with white particles. 294

Figure 5.98. Photomicrographs of BRAZ sample: D and F in XPL, A, B, C and E in PPL. A) Green celadonite (Cel); B) Green celadonite (cel) associated with quartz (qz) forming radial texture; C) greenish material in PPL and D) the same material in XPL showing anisotropic radiating fibrous structures; E) Beige volcanic glass (red arrows); F) Aggregate particle composed of quartz (qz) and chalcedony (chc).	295
Figure 5.99. Basalt in BRAZ-F1 sample. Photomicrograph (A and B1) in PPL and BSE image (C2) showing the points of analysis.	296
Figure 5.100. Sample BRAZ-F2 (Basalt). Photomicrograph (A) in PPL and BSE image (B) with respective points of analysis.	297
Figure 5.101. Basalt in BRAZ-F2. Photomicrograph (A1, B1) in PPL and BSE image (A2, B2) and respective points of analysis.	298
Figure 5.102. Macroscopic photos of the CAN aggregate with different fractions: A) General view; B) detail of one of the fractions containing white minerals.	299
Figure 5.103. Microphotographs of CAN sample. Photo A, C, D and E in XPL. Photos B and F in PPL. A) Subophitic texture; B) Plagioclase being altered in green chlorite; C) vesicle with chlorite; D) Vesicle filled with calcite; E) Vein of calcite; F) Green volcanic glass in vesicles.	300
Figure 5.104. Basalt in CAN-F1 (Basalt). Photomicrographs (A1, A2 and B1) in PPL and BSE image (B2), with indication of the points of analysis.	301
Figure 5.105. Basalt in CAN-F1. Photomicrographs (A1, B) in PPL, BSE image (A2) and respective points of analysis.	302
Figure 5.106. Macroscopic photos of the MOZ aggregate with different fractions: A) General view; B) detail of one of the fractions with white and orange surfaces.	303
Figure 5.107. Photomicrographs of MOZ rhyolite. B in XPL, A in PPL. A) Brownish area corresponds to volcanic glass; B) Presence of tridymite with a wedge habit.	303
Figure 5.108. Rhyolite in MOZ. Photomicrograph (A1) in PPL, BSE image (A2) and respective points of analysis.	304
Figure 5.109. Macroscopic photos of the NOR aggregate with different fractions: A) General view; B) detail of one of the fractions with white areas (red arrow).	305
Figure 5.110. Photomicrographs of NOR sample: B, C, D and F in XPL, A and E in PPL. A) and B) Plagioclase with epidotes and chlorite; C) Amphibole after pyroxene; D) Vesicles filled with chlorite and rimmed by cryptocrystalline quartz; E) and F) Vesicles filled with calcite, epidote and chlorite.	306
Figure 5.111. Basalt in NOR sample. Photomicrograph (A1, B) in PPL, BSE image (A2) and respective points of analysis.	307
Figure 5.112. Basalt in NOR sample. Photomicrograph (A) in PPL, BSE image (B) and respective points of analysis.	308
Figure 5.113. Macroscopic photos of the TK aggregate with different fractions: A) General view; B) detail of one of the fractions with white dots and the surfaces lined by a beige or red colour material.	309
Figure 5.114. Photomicrographs of the Turkey sample: C, D and E in XPL, A, B and F in PPL. A) Plagioclase phenocryst with glass inclusions; B) Olivine crystals completely replaced by iddingsite; C) Calcite pseudomorph; D) Calcite filling a vesicle; E) xenolith containing plagioclase, clinopyroxene and opaque minerals; F) Groundmass containing abundant brown volcanic glass.	310

Figure 5.115A. TK andesite. Photomicrograph (A) in PPL and BSE image (B) with locations of the EDS spectra of volcanic glass (E132-E134).	311
Figure 5.115B. TK andesite: EDS spectra of volcanic glass (E132-E134).	311
Figure 5.116. TK andesite. Photomicrograph (A) in PPL and BSE image (B) and respective points of analysis.	312
Figure 5.117. TK andesite. Photomicrograph (A) in PPL and BSE images (B1 and B2) and respective points of analysis.	313
Figure 5.118. TK andesite. Photomicrograph (A) in PPL and SEM backscattered electron image (B) showing the points of analysis.	314
Figure 5.119. Expansion results of the AMBT (CSA A23.2-25A) concerning the BRAZ aggregate..	315
Figure 5.120. Expansion results of the AMBT (CSA A23.2-25A) concerning the CAN aggregate.	316
Figure 5.121. Expansion results of the AMBT (CSA A23.2-25A) concerning the MOZ aggregate.	317
Figure 5.122. Expansion results of the AMBT (CSA A23.2-25A) concerning the NOR aggregate.	318
Figure 5.123. Expansion results of the AMBT (CSA A23.2-25A) of the TK aggregate..	319
Figure 5.124. Photomicrographs of BRAZ mortar bar. All Photos in PPL. A) Crack with brownish gel within a basaltic aggregate particle that extends to the cement paste; B) Crack with brownish gel within another basaltic aggregate particle that extends into the cement paste; C) Crack with volcanic glass inside the aggregate particle; D) Crack with gel limited to another aggregate particle and a void also containing gel; E) Void partially filled with brownish gel; F) Pore lined by ettringite crystals.	320
Figure 5.125. Photomicrographs of CAN mortar bar. All Photos in PPL. A) Cracks in the cement paste; B) Crack within a basaltic aggregate particle, empty and extending into the cement paste; C) Cracks and a void filled with brownish material (red arrow).	321
Figure 5.126. Photomicrographs of Spratt (siliceous limestone) mortar bar, used as reference in the laboratory tests. All photos in PPL. A) Crack crossing an aggregate particle and extending into the cement paste, lined by gel; B) Crack with gel crossing the cement paste and an aggregate particle.	322
Figure 5.127. Photomicrographs of MOZ mortar. All photos in PPL. A) Very fine cracks in the cement paste; B) Crack filled with gel within the rhyolite particle that extends into the cement paste, where it is lined by gel; C) The extension of the same crack shown in B), crossing the cement paste and cutting some aggregate particles; D) Another crack within the rhyolite particle with gel that extends into the cement paste and crosses another aggregate particle; E) Cracks, one extending to the pore and another crossing an aggregate particle, both containing gel; F) Pore connected with a rhyolite particle by a crack.	323
Figure 5.128. Photomicrographs of NOR mortar. All photos in PPL. A) Minor cracks in the cement paste; B) Crack with a brownish material within a basaltic particle; C) Cracks with a brownish material within a basaltic particle that extended into the cement paste); D) two pores filled with brownish material.	324
Figure 5.129. Photomicrographs of TK mortar. All photos in PPL. A) Large crack within the aggregate particle partly filled with gel; B), C), D) and E) Cracks with gel within the aggregate particles extending into the cement paste and connecting to other particles; F) Gel in the interface of the aggregate particle with the cement paste, with continuity into the cement paste.	325

Figure 5.130. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the BRAZ aggregate.	327
Figure 5.131. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the CAN aggregate.	328
Figure 5.132. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the MOZ aggregate.	329
Figure 5.133. Expansion results of the CPT method test at 35°C (CSA A23.2-14A, 2015) concerning the NOR aggregate.	330
Figure 5.134. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the TK aggregate.	331
Figure 5.135. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the SPRATT aggregate.	332
Figure 5.136. GPT performed in different polished concrete sections at week 19. A) concrete setion with BRAZ aggregate; B) Detail of one aggregate particle (BRAZ).	333
Figure 5.136 (continued). GPT performed in different polished concrete sections at week 19. C) Concrete section with CAN aggregate; D) Detail of the cement paste (CAN); E) Concrete section with Spratt aggregate; F) Detail of the concrete (Spratt).	334
Figure 5.137. GPT performed on different polished concrete sections at week 19. A) concrete section with MOZ aggregate; B) Detail of some aggregate particles (MOZ) with deposits of gel	334
Figure 5.137 (continued). GPT performed on different polished concrete sections at week 19. C) Concrete section with NOR aggregate; D) Detail of the cement paste (NOR); E) Concrete section with TK aggregate; F) Detail of the concrete (TK) with extensive deposits of gel on one of the aggregate particles.	335
Figure 5.138. Photographs of TK concrete prisms observed under the stereobinocular microscope. A) Open crack with some gel in an aggregate particle, extending into the cement paste; B) Open crack in an aggregate particle with reaction product and outlining the particle (red arrows); C) an aggregate particle with a rim of gel filling the interfacial zone with the cement paste; D) cracks in the cement paste and in one of the aggregate particles.	337
Figure 5.139. Photographs of BRAZ concrete prism. A) Open crack within the aggregate particle (red arrows); B) Open crack within another aggregate particle.	337
Figure 5.140. Photographs of MOZ concrete prism. A) Closed crack within the aggregate particle (red arrows); B) Open and closed crack (red arrow in the right) within the aggregate particle.	338
Figure 5.141. Photographs of Spratt concrete prisms. A) Several cracks within an aggregate particle that extend into the cement paste, containing reaction product in both places (red arrows); B) Crack with reaction product within an aggregate particle that continues to the cement paste and connects to a void filled with ASR gel; C) different voids with ASR gel; D) Debonded aggregate particle and crack inside the particle (red arrows).	338
Figure 5.142. Photomicrographs of BRAZ concrete prism. All photos in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction.	339
Figure 5.142 (continued). Photomicrographs of BRAZ concrete prism. All photos in PPL. C), D), E) and F) tiny cracks with brownish material (gel?) in the interfacial zone between the aggregate particles and the cement paste and extending into the cement paste.	340
Figure 5.143. Photomicrographs of Spratt reference concrete prism. All photos are in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction; C)	341

Cracks with brownish material in the cement matrix; D) Void partly filled with brownish material (gel?).

Figure 5.144. Photomicrographs of MOZ concrete prism. All photos are in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction; C) Cracks in the interface zone between an aggregate particle and the cement matrix; D) Very fine cracks in the cement paste and an empty void. 342

Figure 5.145. Photomicrographs of the TK concrete prism. All photos are in PPL. A) Brownish material in a crack outlining an aggregate particle; B) Cracks in the cement matrix connecting some grains of the sand fraction and a void; C) Cracks within the aggregate particle; D), E) and F) Cracked yellow-brownish material located in different locations of an aggregate particle at the boundary between particle and cement paste. 343

Figure 6.1. Correlation between CPT and AMBT results. The yellow dot colour represents all the samples that contain volcanic glass. The grey vertical line represents the limit of 0.04% expansion for the CPT test and the grey horizontal line the limit of 0.10% for the AMBT. 355

Figure 6.2. Correlation between the SiO₂ composition of volcanic glass and expansion tests: A) Glass composition vs AMBT and B) Glass composition vs CPT. 356

Figure 6.3. Correlation between one-year CPT expansion and DRI results. Yellow dots correspond to the test specimens incorporating volcanic sand fractions. 359

Figure 6.4. Correlation between the gel formation rating obtained in the GPT and the DRI. 360

List of Tables

Table 2.1. International Conferences on Alkali-Aggregate Reaction in Concrete.	12
Table 2.2. Potentially alkali-reactive natural constituents in rocks / concrete aggregates (adapted from Kerr, 1977; Katayama and Kaneshige, 1986; Sims and Nixon, 2003; Blight and Alexander, 2011; Thomas et al., 2013b; Ramos, 2013; RILEM AAR-1.1, 2016).	18
Table 2.3. Pessimism” proportions of silica minerals and volcanic glasses in mortar bars (adapted from Katayama, 1997b; Katayama et al., 2021).	22
Table 2.4. Procedures for the diagnosis of ASR according to different authors.	29
Table 2.5. Classification of the cracks based on their width on site according to Godart et al. (2013).	32
Table 2.6. Signs of ASR, appearance, preferential location and causes.	35
Table 2.7. Methods of examination and the different features observed based on Ramos (2013) and Poole and Sims (2016).	39
Table 2.8. Environmental classes (AAR-7.1, 2016).	40
Table 2.9. Aggregate beneficiation (ACI 1998; Alexander and Mindess, 2005; Farny and Kerkhoff, 2007).	43
Table 2.10. Alkali limits for different aggregate reactivity categories (AAR-7.1, 2016).	44
Table 2.11. Chemical composition of GGBFS from three countries (Özbay et al., 2016).	48
Table 2.12. Chemical composition of silica fume from the production of silicon metal and 75% ferrosilicon alloy (Hjorth, 1982).	54
Table 2.13. Chemical composition, benefits and level required to prevent ASR for each type of SCMs.	57
Table 3.1. Summary of the petrographic characteristics of the concrete pavement in Curuzú Cuatiá city.	63
Table 3.2. Summary of the petrographic characteristics of the concrete pavement in the airport.	65
Table 3.3. Chemical composition of the gel, aggregate particles and OPC (Ólafsson, 1992).	71
Table 3.4. Results of the surveys were conducted in 2003, 2005 and 2006 (Guðmundsson, 2008).	72
Table 3.5. Results of the study conducted by LNEC on the basaltic aggregate and concrete cores (Reis et al., 1996).	76
Table 3.6. Results of the study of the concrete cores and aggregates (Fernandes et al., 2015; Medeiros et al., 2014a, 2015a and b and 2016).	77
Table 3.7. Summary of mixtures used in Lomas Boulevard experimental pavement (Folliard et al., 2006).	80
Table 3.8. Petrographic examination results of the concrete cores from the experimental Pavement.	81
Table 3.9. Petrographic characteristics of the volcanic rocks for each setting (Wilson, 1989; Winter, 2001; Frost and Frost, 2014).	113
Table 4.1. Aggregate samples per country.	126
Table 4.2. Aggregates are used exclusively in the AMBT and CPT.	128

Table 4.3. Purpose of the petrographic examination of aggregates as in international and national standards, specifications, recommendations and according to Blight and Alexander (2011) and Ingham (2011).	131
Table 4.4. Rock types and potentially alkali-reactive constituents of each rock type according to RILEM AAR 1.1 (2016).	132
Table 4.5. Tholeiitic Basalts Vs Alkali basalts.	140
Table 4.6. Further subdivisions of the TAS diagram.	141
Table 4.7. Comparison of different accelerated mortar bar test methods according to ASTM C1260 (2014), CSA A23.2-25A (2019), and RILEM AAR-2 (2016).	143
Table 4.8. Comparison of different concrete prism test methods according to ASTM C1293 (2020), CSA A23.2-14A (2019), and RILEM AAR-3 (2016).	146
Table 4.9. Petrographic features and weighing factors are used in the determination of DRI (Villeneuve, 2011; Villeneuve et al., 2012; Fournier et al., 2015).	151
Table 4.10. Different ranges of DRI values are associated with the typical petrography features of deterioration (Villeneuve, 2011; Villeneuve et al., 2012; Fournier et al., 2015).	154
Table 4.11. Petrographic examination of concrete thin sections (ASTM C 856, 2020).	160
Table 4.12. Aspects to observe in aggregates for alkali-silica reaction (ASTM C 856, 2020)	161
Table 4.13. Summary of the methods and equipment used in the present work	162
Table 5.1. Country, region and code names were given to the different aggregates studied.	165
Table 5.2. Bulk chemical composition of the ocean islands volcanic aggregates.	177
Table 5.3. Results of the calculation of the ocean islands volcanic aggregates CIPW norm (wt %).	178
Table 5.4. Chemical classification of each rock sample based on the TAS diagram.	180
Table 5.5. Sample CANY1. EPMA-WDS results concerning the composition of a yellowish zeolite crystal whose composition is compatible with natrolite (Figure 5.13).	186
Table 5.6. Sample CANY1 EPMA-WDS results of the dark-brown volcanic glass in Figure 5.14	187
Table 5.7. Sample HW1. EPMA-WDS results of the analyses of volcanic glass.	194
Table 5.8. Sample HW3. EPMA-WDS results concerning the composition of volcanic glass (1-4).	195
Table 5.9. Sample HW5. EPMA-WDS results concerning the composition of volcanic glass (1 and 2, Figure 5.22).	196
Table 5.10. Sample HW6. EPMA-WDS results concerning the composition of volcanic glass (1 and 2, Figure 5.23).	197
Table 5.11. Sample HW7. EPMA-WDS results concerning the composition of volcanic glass (1-5).	198
Table 5.12. Sample HW7. EPMA-WDS results concerning the composition of volcanic glass (1-6).	199
Table 5.13. Sample ICL1-F1. EPMA-WDS results of zeolite (1,2).	205
Table 5.14. Sample ICL1-F2. EPMA-WDS results of plagioclase (1), quartz (2) and volcanic glass (3) in dacite.	206

Table 5.15. Sample ICL1-F2. EPMA results of of quartz (1 and 4) and alkali feldspar (2 and 3).	208
Table 5.16. Sample ICL1-F3. EMPA-WDS results of quartz (1, 2, 5, 6, 7 and 8,) and alkali feldspar (3 and 4).	209
Table 5.17. Sample ICL2-F2 EMPA-WDS results of the yellowish material (1, 2 and 3).	214
Table 5.18. Sample ICL4-F3 EPMA-WDS results of volcanic glass (1- 3).	219
Table 5.19. Sample ICL4-F4. EMPA-WDS results of possibly smectite (1-2) and of volcanic glass (3-6).	220
Table 5.20. Sample ICL4-F4. EPMA-WDS results of volcanic glass (1-5).	221
Table 5.21. Sample NZ1. EPMA-WDS analyses of zeolite (1-4) filling a vesicle.	227
Table 5.22. Sample NZ1. EMPA-WDS results of chlorite–smectite minerals (C/S) (1-3) and volcanic glass (4-8).	229
Table 5.23. Sample NZ3. EMPA-WDS analyses of volcanic glass (1-3) of figure 5.51.	232
Table 5.24. Sample NZ3. EPMA-WDS analyses of volcanic glass (1-4) of figure 5.52.	233
Table 5.25. Sample NZ3. EMPA-WDS analyses of volcanic glass (1-4) of figure 5.53.	234
Table 5.26. EPMA results of volcanic glass – palagonite (1- 6).	263
Table 5.27. EPMA results of volcanic glass (1-14) (oxides in %).	267
Table 5.28. EPMA results of volcanic glass (1-5).	268
Table 5.29. Bulk chemical composition of the continental volcanic aggregates.	291
Table 5.30. Results of the calculation of the continental volcanic aggregates CIPW norm (wt %).	291
Table 5.31. Chemical classification of each rock sample based on the TAS diagram.	293
Table 5.32. Sample BRAZ-F1. EPMA indicative results of volcanic glass in BRAZ-F1 sample.	296
Table 5.33. Sample BRAZ-F2. EMPA results of possibly chlorophaeite (?) (1 and 2).	297
Table 5.34. Sample BRAZ-F2. EMPA results of possibly chlorophaeite? (1-2) and silica minerals (3-4).	298
Table 5.35. Sample CAN-F1. EPMA results of volcanic glass (1-2; 4-5) and pyroxene (3).	301
Table 5.36. Sample CAN-F1. EPMA results of volcanic glass (1-4).	302
Table 5.37. Sample MOZ. EMPA results of volcanic glass (1-4).	304
Table 5.38. Sample NOR. EMPA results of epidote (1-3).	307
Table 5.39. Sample NOR. EMPA results of epidote (1) and silica minerals (2).	308
Table 5.40. Sample TK. EPMA results of inclusions of volcanic glass (1-3) from Figure 5.116.	312
Table 5.41. Sample TK. EPMA results of volcanic glass: groundmass (1, 2, 4) and inclusions in the plagioclase (3, 5-9) from Figure 5.117.	313
Table 5.42. Sample TK. EMPA results of volcanic glass (1-4) from Figure 5.118.	314
Table 5.43. Results of the GPT after 19 weeks of testing	333

Table 5.44. Detailed results (number of counts multiplied by the weighing factors) of reaction features for each sample at the end of one year of testing.	334
Table 5.45. Concrete condition and degree of deterioration based on the DRI results based on Villeneuve, (2011); Villeneuve et al., (2012); Fournier et al., (2015). Spratt and GBS area reference aggregates	334
Table 6.1. Results from all the methods used with the different aggregates. The results highlighted in blue indicate the samples classified as reactive in all laboratory expansion tests and by petrography.	345
Table 6.2. Comparison of the results obtained in DRI for sand aggregates and GPT.	360

CHAPTER 1

INTRODUCTION

1.1. Scope of the work

Concrete is one of the most widely used building materials of our time. According to Coutinho (1988), the oldest known concrete dates back to 5,600 B.C. on the ground floor of a house, located on the banks of the Danube River, in the former Yugoslavia. However, the first concrete-like structures were built by the Nabataea traders or Bedouins who occupied southern Syria and northern Jordan regions in around 6500 B.C. By 700 B.C., they were building concrete floors, and underground waterproof cisterns (e.g., <https://www.nachi.org/history-of-concrete.htm>).

Concrete is composed of coarse and fine aggregates, a binder (cement and other supplementary cementitious materials), water and eventually chemical admixtures. The aggregates are considered a fundamental element in the construction sector representing about two-thirds of the concrete composition. However, some aggregates can react when in contact with the cement paste pore solution causing deterioration in the concrete. One of these types of deterioration is known as the alkali-silica reaction (ASR). It is an expansive chemical reaction that occurs between the alkali and hydroxyl ions present in the cement paste and the reactive forms of silica in the aggregates. The reaction leads to the formation of an expansive gel which causes expansion, cracking and an early deterioration of the concrete structures. This reduces the durability, safety and performance of the concrete structures.

Volcanic rocks are often used as concrete aggregates mainly because of their local availability/abundance. This is mostly the case for volcanic islands that do not have other options besides using what they have in their territory. Basalts are often one of the most common rocks in these cases and are usually referenced in the literature as good aggregates for concrete purposes. According to Korkanç and Tugrul (2004), basalts improve the strength and the quality of concrete. However, the potential alkali reactivity of basalts is still not very well known and understood. Even today, this subject remains a source of discussion among researchers, whether they are considered reactive or not. It seems that their reactivity varies from country to country, from source to source and according to the test methods used. Also, Fernandes et al. (2015) indicate that the regional geological history of the rock plays an important role in its reactivity. The reactivity of basalts has been attributed to the presence of volcanic glass (Katayama et al., 1989; Wakizaka, 2000; Korkanç and Tugrul, 2004; Wigum et al., 2007; Munhoz et al., 2008; Marfil et al., 2013; RILEM AAR-1-1, 2016; Madsen et al., 2019), devitrified volcanic glass (RILEM AAR-1-1, 2016), different types of silica such chalcedony, opal, cryptocrystalline and microcrystalline silica (Katayama et al., 1989; Wakizaka, 2000; Wigum et al., 2007; Munhoz et al., 2008; Marfil et al., 2013; RILEM AAR-1-1, 2016; Madsen

et al., 2019) and according to some authors to swelling clay minerals (Marfil et al., 2013; Madsen et al., 2019).

There are some reports of reactive basalts in concrete structures from Argentina (Marfil et al., 1998; Marfil et al., 2005; Marfil and Maiza, 2006; Milanesi et al., 2008; Maiza et al., 2010 and Madsen et al., 2019) and Iceland (Katayama et al., 1996; Guðmundsson and Ólafsson, 1999). In Argentina, the majority of the cases are related to the deterioration of concrete pavements where basaltic coarse aggregates were used together with siliceous sand, where both fractions show petrographic features of deterioration such as reaction rims, gel and cracks. In Iceland, severe ASR problems started to appear in several houses during the 1970s. This was due to the use of reactive aggregates with high amounts of rhyolitic rocks, altered basalts and unwashed sea dredged material (Guðmundsson and Ólafsson, 1996) together with high alkali cement and favourable environmental conditions; all of these factors triggered ASR in the Icelandic concretes (Guðmundsson and Ólafsson, 1999; Lindgård et al., 2017). Also, basalts have been considered reactive when subjected to certain laboratory tests, especially when they were used in the AMBT method. This was reported by several researchers from countries such as Argentina (Batic et al., 1994), Australia (Shayan and Quick, 1988), Brazil (Munhoz, 2007; Munhoz and Cincotto, 2008), Czech Republic (Seidlová et al., 2012), Iceland (Wigum et al., 2007) and in the USA (Hawaii) (Thomas et al., 2013a; Robertson and Shen, 2018).

Regarding the different test methods that are usually used to evaluate the potential alkali-reactivity of concrete aggregates, the petrographic method is always the first step to be performed (RILEM AAR-0, 2016). According to Lindgård et al., (2010), this method can give faster results and is generally rather effective in identifying reactive materials. The expansion laboratory tests are the next step to follow in accordance with RILEM AAR-0 (2016). The rapid screening tests that include the accelerated mortar bar tests (AMBT) (ASTM C 1260 (2014) or RILEM AAR-2, Nixon and Sims, 2016) are commonly first performed. Then, the concrete prism expansion tests (CPT) that comprise the RILEM AAR-3 (1 year - 38°C) and RILEM AAR-4.1 (20 weeks – 60°C) (Nixon and Sims, 2016) are conducted depending on the results of the first step. However, contradictory information has been obtained regarding the AMBT and the CPT. Nixon and Fournier (2017) consider that several aggregates give erroneous and misleading results in the AMBT when compared to the more accurate and realistic CPT. Santos Silva et al., (2016) affirms that the AMBT should not be used for testing igneous rocks and recommend in the specific case of basalts to apply a slow CPT with a test extension until two years. On the other hand, Lindgård et al. (2010) report good results regarding the AMBT method through the EU “PARTNER” project and the inter-laboratory trials conducted under the auspices of the

International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM).

Besides the recommended test methods by RILEM, other methods were used in the assessment of the potential alkali reactivity of the volcanic aggregates. These methods included the DRI (Damage Rating Index) and GPT (Gel Pat test). According to Sanchez et al. (2015), the DRI is a semi-quantitative petrographic method for assessing damage in polished concrete sections that has been increasingly used around the world. It is frequently used in Canada for the condition assessment of concrete structures in which there is suspicion of deterioration. The GPT is less commonly used, being a practice in some countries like the UK (Sims, 2017), Canada (Bérubé and Fournier, 1993; Villeneuve, 2011 and Tremblay et al., 2012), and is described in some works in Spain (Lanza and Alaejos, 2012) and Czech Republic (Fernandes et al., 2017). It evaluates the gel formation at the surface of the reactive aggregate particles when polished concrete sections are immersed in a 1N NaOH solution at 38°C or 80°C.

The present work aims to study the potential alkali-silica reactivity of a variety of basalts from different parts of the world through the use of different test methods (petrographic characterization, the AMBT and the CPT). The andesites present in this study were used as control aggregates of volcanic origin, due to their known reactivity.

1.2. Objectives

To better understand the reactivity of volcanic aggregates, especially basalts, the main objectives of this thesis are to:

- assess the potential alkali-reactivity of basaltic aggregates, highlighting the comprehensive study of their chemical, mineralogical and textural composition/characteristics. This analysis should be developed by petrographic methods, either in the study of the aggregates or in the reaction with cement paste that occurred during the laboratory tests.
- improve the current knowledge on the behaviour of basalts when incorporated into concrete, particularly in the context of oceanic islands. In this context, the expected results should provide new elements (e. g. petrographic methods and laboratory tests) capable of clarifying contradictory information obtained with different methods for evaluating the alkali-reactivity of volcanic aggregates.

- obtain a better knowledge of the Azorean aggregates and their relation with other volcanic aggregates around the world and thereby contribute to better performance and durability of the concrete used in volcanic regions.

To ensure the fulfilment of the above objectives, volcanic aggregates from different geological environments around the globe were selected and processed, with special emphasis on islands, and subjected to different evaluation methods. These methods will characterize the chemical and mineralogical composition of the rock and correlate it with the various processes that occur in ASR. In addition to the evaluation of the potential alkali-reactivity of the studied aggregates, the expected results will allow it to make correlations between nature, age and origin of volcanic rocks.

1.3. Organization of the thesis

This thesis is organized into seven chapters:

Chapter 1 – Introduction

Chapter 2 – Deterioration of concrete by alkali-silica reaction

Chapter 3 – Alkali-silica reaction in volcanic aggregates

Chapter 4 – Materials and methods

Chapter 5 – Results

Chapter 6 – Analysis and discussion

Chapter 7 – Conclusions

Chapter 1 makes the introduction to the problem of alkali-silica reactions in volcanic aggregates and describes the objectives and organization of the thesis.

Chapter 2 presents the state of the art concerning the alkali-silica reaction. It provides the definition and historical background is given, and then describes the occurrence, diagnosis and preventive measures related to the pathology.

Chapter 3 reports some case studies either of concrete structures affected by ASR where volcanic aggregates were the cause of the concrete deterioration and different test methods where volcanic aggregates were considered potentially reactive. In another section of this chapter, a correlation is presented between the volcanic aggregates petrography and their

tectonic setting, while the deleterious constituents of volcanic rocks are described in the final part of this chapter.

Materials and methods are described in Chapter 4. The materials section presents the aggregates selected for this study. In the methods part, the different methodologies used in aggregates, mortar and concrete testing are presented. A SWOT analysis was conducted to highlight the strengths, weaknesses, opportunities and threats of each method used. Also, a comparison is made between the limits used for the AMBT and CPT specified by the RILEM recommendations and the ASTM and CSA standards.

The results are presented in Chapter 5. This chapter is organized into sites/samples from Islands and sites/samples from Continental regions. The first part of each site/sample describes a general geological setting for each country from which the samples come. Following the geological setting, a characterization of volcanic aggregates is done that includes the petrographic examination. Next, mortar and concrete studies are described and presented in the form of graphics, where the development of the expansion is shown as a function of time, in accordance with the current standards and recommendations. In addition, a post-mortem petrographic examination was conducted after the completion of the expansion tests. This petrographic examination was carried out by using a polarizing microscope, and the DRI method was also used in half of the concrete prisms where petrographic features of deterioration were identified. Gel Pat Tests was performed on concrete prisms manufactured at Laval University and also with the Azorean aggregates. The development of the gel was monitored at the surface of the test prisms at regular intervals.

Chapter 6 presents the analysis and discussion of the results. Different subjects are analyzed and discussed that include the petrography of the aggregates, rock suites and geological settings; post-mortem petrography of mortar/concrete specimens and results of laboratory tests and methods.

In the last chapter, main conclusions and future developments are drawn based on the results obtained and in comparison with the case studies exposed in Chapter 3.

CHAPTER 2

DETERIORATION OF CONCRETE BY ALKALI SILICA REACTION

2.1. The definition of alkali-aggregate reaction

The alkali-aggregate reaction (AAR) is a chemical reaction that occurs in either mortar or concrete (Godart et al., 2013) and involves the hydroxyl (OH^-) and the alkali (Na^+ and K^+) ions within the cement paste pore solution and certain reactive components present in the aggregates.

Gillott (1975) proposed to divide the AAR into three groups:

- Alkali-silica reaction (ASR);
- Alkali-carbonate reaction (ACR);
- Alkali-silicate reaction.

This subdivision took into account the components that were considered reactive and the reaction mechanisms.

Currently, many countries consider only two main groups (Godart et al., 2013; Leemann et al., 2015): (1) ASR and (2) ACR. Godart et al. (2013) defend that the alkali-silicate reaction is recognized as a slow/late type of ASR. Poole (2017) states that there is some compelling evidence that ACR and alkali-silicate reactions are just variants of ASR.

ASR is considered the most common type of AAR and the more widespread whilst ACR is the least common and generally restricted to some regions of the world.

In general terms, the ACR occurs between alkali ions in the cement paste pore solution and certain argillaceous dolomitic limestone aggregates (Godart et al., 2013). The reaction is usually accompanied by dedolomitization and the affected aggregate particle expansion leads to extensive concrete expansion and cracking (Thomas et al., 2013b). On the other hand, ASR occurs between the alkali hydroxides from Portland cement and/or other sources and certain siliceous rocks or minerals, such as opaline silica, chert, microcrystalline quartz, and acidic volcanic glass, recycled glass, etc. present in some aggregates. The reaction produces an alkali-silica gel that causes expansion and cracking of the mortar/ concrete (Godart et al., 2013).

2.2. History of ASR

The ASR was first identified in the 1930s, in the state of California, in the United States of America (USA), where cracking and concrete expansion started to appear in school buildings, bridges, road pavements and sea walls. Thomas Stanton (Figure 2.1) a material engineer from the California State Division of Highways reported this problem and published an article in the

Proceedings of the American Society of Civil Engineers (Stanton, 1940). He discovered that the deterioration of concrete was due to a reaction between the alkalis present in the Portland cement and siliceous rock aggregates. He found out that the problem was triggered by two conditions: the presence of certain types of mineral components in the aggregates and cement alkalis exceeding a certain minimum threshold percentage. His investigation revealed that the expansion of mortar bars was influenced by certain conditions: the alkali content of the cement, the type and amount of the reactive silica in the aggregate, the availability of moisture, and temperature. He also verified that expansion was negligible when the alkali content of the cement was below 0.60% $\text{Na}_2\text{O}_{\text{eq}}$. Stanton further investigated the use of preventive measures and verified that a sufficient quantity of pozzolan used as a replacement for Portland cement eliminated deleterious expansion while other replacements did not produce the same effect (Stanton 1950). Thomas et al. (2011) indicate that other studies were conducted in the same period that recognized the efficiency of other supplementary cementing materials (SCMs) such as fly ash and slag, in reducing expansion due to ASR.

Since Stanton's discovery, numerous structures such as dams, pavements and bridges in the USA were diagnosed with suffering ASR (Thomas et al., 2013b).

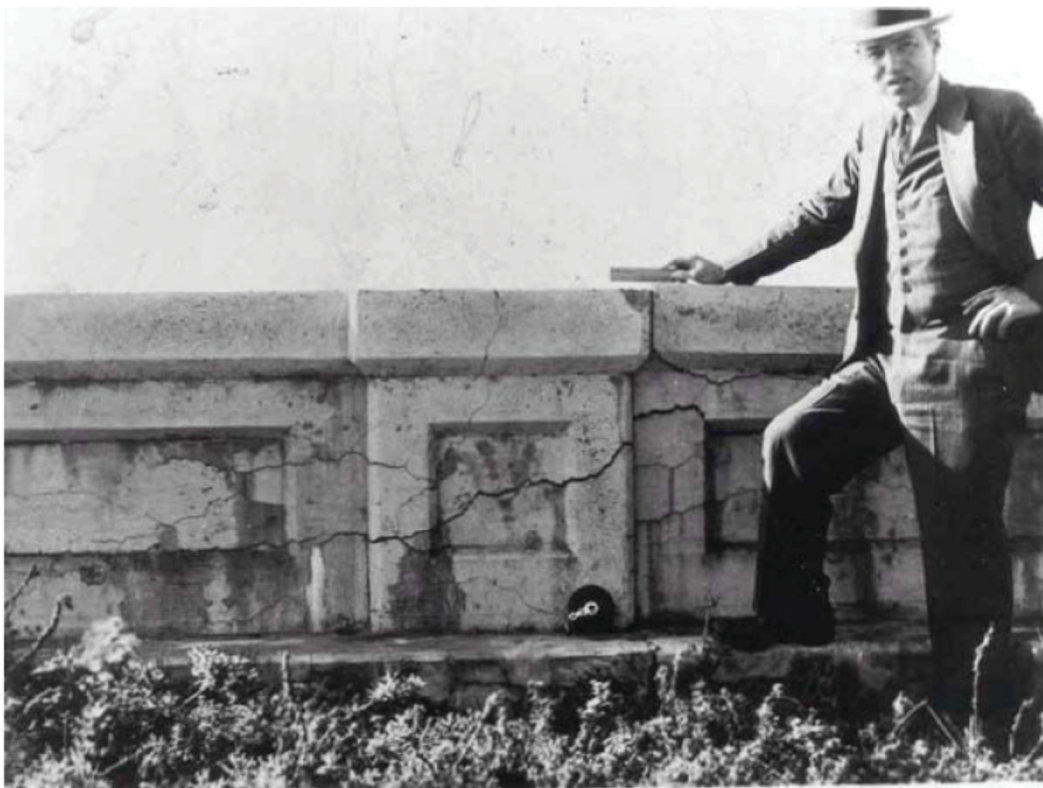


Figure 2.1. Thomas Stanton standing beside a Bridge Parapet Wall with signs of ASR (Thomas et al., 2013b)

After the identification of ASR in the USA in the 1940s, several other cases were reported throughout the world in the following decades. Some examples are described in the following paragraphs:

- In Denmark, the ASR was first identified in 1951 by Poul Nerenst who visited the USA and observed ASR deterioration in concrete. The Danish National Institute of Building Research (DNIBR) then started a preliminary investigation of several concrete structures in the country and concluded that they had the same problem as the USA (Lindgård et al., 2017).
- In Japan, Katayama and Kaneshige (1986) mentioned that the discovery of ASR is reported by Kondo and co-authors in 1951. Also, Diamond (1992) refers to the same authors in his bibliography list describing that the authors discussed about two bridges damaged by ASR, wherein the most damaged part was volcanic ash used as an aggregate.
- In Iceland, ASR was first mentioned in 1954 when a report from the Icelandic Building Research Institute (IBRI) referred that ASR was the possible cause of damage to concrete structures in the country (Wigum et al., 2007). During the 1970's Iceland suffered a severe problem with the use of a new sea-dredged source of aggregates (Guðmundsson and Ólafsson, 1996, 1999, 2002), being only in 1976 given the first proof that ASR was the cause of concrete house deterioration in Iceland (Ólafsson, 1992; Wigum et al., 2007).
- In Canada, the first reported case of ASR was identified in the mid of 1950s in the Hurdman bridge from Ottawa which was built in 1906 and demolished in 1987 (Rogers, 1989; Rogers et al., 2000). Swenson (1957) described that two deck sections (north and south) presented different degrees of deterioration being affected by different types of cement aggregate reactions.
- In the Russian Federation, the first examples start to appear at the beginning of the 1960s. Some of the recognized cases of ASR in the country are house footing structures, railway sleepers, port facilities, among others (Falikman and Rozentahl, 2017).
- In New Zealand, only in 1970 was identified the first known case of ASR in a structure, Te Henui Bridge (St. John, 1989; St. John, 1992; Shayan and Freitag, 2017) where andesite was the reactive aggregate (St. John, 1992). However, ASR was recognized to be a problem in New Zealand by the Ministry of Works and Development since 1943 (St. John, 1992; Shayan and Freitag, 2017).

- In Brazil, CESP (took into consideration the occurrence of ASR in their constructions since the 1960s (Zoilo, 2010). It began in 1963 with the Jupia dam (Hasparyk, 1999) where the presence of cracks was noticed in one of the floors which were associated with the gravel used from the Paraná River that contained chalcedony as a reactive phase (Munhoz, 2007). According to Hasparyk (1999), to combat this problem, it was necessary to use preventive measures; first, it was used a low-alkali cement and then 35% pozzolan was used as cement replacement. However, Couto (2008) declares that the first suspicious case of ASR was reported by Kihara and Scandiuzzi in 1985 (1993 in Couto, 2008), in a dam named Apolônio Chaves.
- In France, the first cases were diagnosed in the 1970s in different dams. A bridge and other structures built around 1986 showed the same ASR signs where a siliceous limestone from the Tournai region was used together with a low-alkali cement (0.60% $\text{Na}_2\text{O}_{\text{eq}}$). (Fernandes et al., 2017).
- In the UK, the ASR was first diagnosed in 1976 with extensive cracking in unreinforced concrete foundation blocks at three electricity substations in southwest England (West, 1996). However, in 1971, it was reported that a dam in Jersey Island (The Vale de la Mare dam) had concrete sections discoloured, dampened and cracked, while a displacement of 13 mm was noticed in some places. Some remedial measures were taken (Sims, 2017). This was considered probably the first case of ASR in the UK. As years passed, more concrete structures appeared to be affected by ASR in the UK.
- In Norway, the first report on ASR damage seems to have been in 1978 (Broekmans, 2002; Lindgård et al., 2017). According to Broekmans (2002), this damage was present in a swimming pool and a concrete foundation; however, the report was received with a lot of disbelief and ASR was only confirmed when the rehabilitation of the swimming pool was done.
- In Australia, the first field cases of ASR date back to the beginning of the 1980s. However, a research program began much earlier through the work in mortar bars and different aggregates conducted between the 1940s and 1950s by Harold Vivian, who played a major role in the Australian knowledge of ASR (Shayan and Freitag, 2017).
- In Italy, the first cases of ASR are related to industrial floors at the beginning of the 1980s (Baronio and Berra, 1989). Rossetti (1981) described one case on the Adriatic coast where he verified the presence of several pop-outs on a concrete industrial floor. In half a square meter, he counted about 200 pop-outs, with a diameter of 10 - 20 mm, some of them with gel exudation and others with white or grey-greenish dust around or

below the pop-outs. The author mentions that the aggregate used seemed to be a fine-grained sandstone with dark grey colour which could be the source of reactivity.

- In Portugal, the first case of ASR seems to appoint to Pracana Dam, in the year 1980. The anomalies and signs of deterioration comprised mainly intense cracking, and displacement (Batista and Gomes, 2012). The potentially reactive aggregates included siliceous materials such as quartzites, meta-mudstones with chalcedony and meta-pelites (Fernandes et al., 2017). Regarding the autonomous archipelagos of Portugal, in the Azores, a concrete airport pavement from one of the islands appeared heavily cracked. A study performed by LNEC identified ASR as being one of the causes of the cracking due to altered basalts (Reis et al. 1996).

The first international conference on alkali-aggregate reaction in concrete, known under the acronym ICAAR, was held in Køge, Denmark, in 1974 with 13 papers represented by the following countries: Denmark, Germany, Iceland, UK and USA (Thomas et al., 2013b). With the increase of ASR cases, ICAAR became an important conference on the subject. These meetings started to happen every year (1974, 1975, 1976), but since London (1992) the conference is held every four years in different cities around the world (Table 2.1). The papers are published in Proceedings and selected articles are published in rated journals.

Table 2.1. International Conferences on Alkali-Aggregate Reaction in Concrete.

Conference	Year	Host	Conference	Year	Host
I	1974	Køge, Denmark	IX	1992	London, UK.
II	1975	Reykjavik, Iceland	X	1996	Melbourne, Australia
III	1976	London, U.K.	XI	2000	Quebec City, Canada
IV	1978	West Lafayette, USA	XII	2004	Beijing, China
V	1981	Cape Town, S. Africa	XIII	2008	Trondheim, Norway
VI	1983	Copenhagen, Denmark	XIV	2012	Austin, USA
VII	1986	Ottawa, Canada	XV	2016	São Paulo, Brazil
VIII	1989	Kyoto, Japan	XVI	2020*	Lisbon, Portugal
*Delayed to 2022 due to COVID-19 pandemic					

Besides the ICAAR, there are also the RILEM Technical Committees (TC) meetings that take place twice a year in different countries. RILEM stands for “Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages” or “International Union of Laboratories and Experts in Construction Materials, Systems and Structures”. It was founded in 1947 with the purpose to promote scientific cooperation in the field of construction materials and structures, where RILEM members exchange their expertise. The first RILEM bulletin which includes 44 issues was first published in 1951, while the first technical committee – 01-CW (winter concreting) was created in 1956. Since then, several RILEM technical committees (TC) have been created on different subjects and the subjects are grouped in different clusters. Regarding AAR, different TC have been created over the years, and some of them already ended their activity (<https://www.rilem.net/>):

- 106-AAR: Alkali-aggregate reaction (no date);
- 191-ARP: Alkali-reactivity and prevention - Assessment, specification and diagnosis of alkali-reactivity (2000-2006);
- 219-ACS: Alkali Aggregate Reaction in concrete structures: performance testing and appraisal (2006-2014);
- 258-AAA: Avoiding alkali aggregate reactions in concrete – Performance-based concept (2014-2020);
- 259-ISR: Prognosis of deterioration and loss of serviceability in structures affected by alkali-silica reactions (2014-2019);
- ARM: Alkali-aggregate reaction mitigation (2020-);
- ASR: Risk assessment of concrete mixture designs with alkali-silica reactive (ASR) aggregates (2020-)

Each TC produces several RILEM recommendations which are used for research and as the basis for international standardization. Some recommendations were created to assist engineers, technicians and other researchers in the field of construction materials regarding AAR. Nixon and Sims (2016) published the RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures - State-of-the-Art Report of the RILEM Technical Committee 219-ACS:

- RILEM Recommended Test Method: AAR-0—Outline Guide to the Use of RILEM Methods in the Assessment of the Alkali-Reactivity Potential of Aggregates
- RILEM Recommended Test Method: AAR-1.1—Detection of Potential Alkali-Reactivity—Part 1: Petrographic Examination Method

- RILEM Recommended Test Method: AAR-2—Detection of Potential Alkali-Reactivity—Accelerated Mortar-Bar Test Method for Aggregates
- RILEM Recommended Test Method: AAR-3—Detection of Potential Alkali-Reactivity—38 °C Test Method for Aggregate Combinations Using Concrete Prisms
- RILEM Recommended Test Method: AAR-4.1—Detection of Potential Alkali-Reactivity—60°C Test Method for Aggregate Combinations Using Concrete Prisms
- RILEM Recommended Test Method: AAR-5—Detection of Potential Alkali-Reactivity—Rapid Preliminary Screening Test for Carbonate Aggregates
- RILEM Recommended Specification: AAR-7.1—International Specification to Minimise Damage from Alkali Reactions in Concrete—Part 1: Alkali-Silica Reaction
- RILEM Recommended Specification: AAR-7.2—International Specification to Minimise Damage from Alkali Reactions in Concrete—Part 2: Alkali-Carbonate Reaction
- RILEM Recommended Specification: AAR-7.3 Preliminary International Specification to Minimise Damage from Alkali-Aggregate Reactions in Concrete—Part 3: Concrete Dams and Other Hydro Structures

In the scope of the same TC, Godart et al. (2013) published a Guide to Diagnosis and Appraisal of AAR Damage to Concrete in Structures - Part 1 Diagnosis (AAR 6.1). Likewise, Fernandes et al. (2016) were the editor of a Petrographic Atlas to be used as guidance and as a complement to the RILEM AAR-1.1 Petrographic Examination Method. This document is entitled “Petrographic Atlas: Characterisation of Aggregates Regarding Potential Reactivity to Alkalis - RILEM TC 219-ACS Recommended Guidance AAR-1.2”.

All of the RILEM recommendations reproduce the state-of-the-art reports at the end of the activities. Though these recommendations can be replaced by new versions with new updates on the subject, as may happen with the ones that are active at present.

2.3. Occurrence

The mechanism of ASR has been studied since it was diagnosed in the 1940s. Since then, a large amount of research has been conducted regarding the causes, effects, mechanisms, prevention (new concrete), and mitigation/repair (existing structures) of ASR.

The occurrence of ASR is controlled by three conditions that occur simultaneously: (1) sufficient quantity of reactive forms of silica in the aggregates; (2) a sufficient concentration of alkali hydroxides in the pore solution of the concrete and (3) sufficient supply of moisture.

However, the following fourth condition is mentioned by Figueira et al. (2019): a source of soluble calcium, such as portlandite, reacts with dissolved silica and forms the deleterious gel.

The increase in temperature is referred to by some authors (Lindgård et al., 2012, Farny and Kerkhoff, 2007; Owsiak et al., 2015) as a factor that affects the rate of the reaction. Structures subject to higher temperatures are more prone to develop ASR than those subject to lower temperatures (Owsiak et al., 2015). However, Farny and Kerkhoff (2007) refer to the results of some studies that confirmed that even at lower temperatures (13°C and 20°C) the expansion was higher, which was related to temperature dependence on different reactive aggregate types. But it seems that most reactive aggregates cause higher expansion at higher temperatures (Farny and Kerkhoff, 2007; Owsiak et al., 2015).

In simple terms, the reaction causes the dissolution of the reactive silica (SiO_2) in the aggregate. It reacts with the alkalis (Na^+ , K^+) and the hydroxyl ions (OH^-) (Figure 2.2.A) to form a viscous gel within the reactive aggregate (Figure 2.2B). The concrete high pH level permits the hydroxyl with associated alkali ions to intrude the reactive silica causing its dissolution and the formation of the secondary alkali-silica gel. The gel absorbs water from the surrounding paste and swells, thus creating pressure within and around the aggregate particles and the hardened cement paste leading the concrete to crack (Deschenes et al., 2009) (Figure 2.2C).

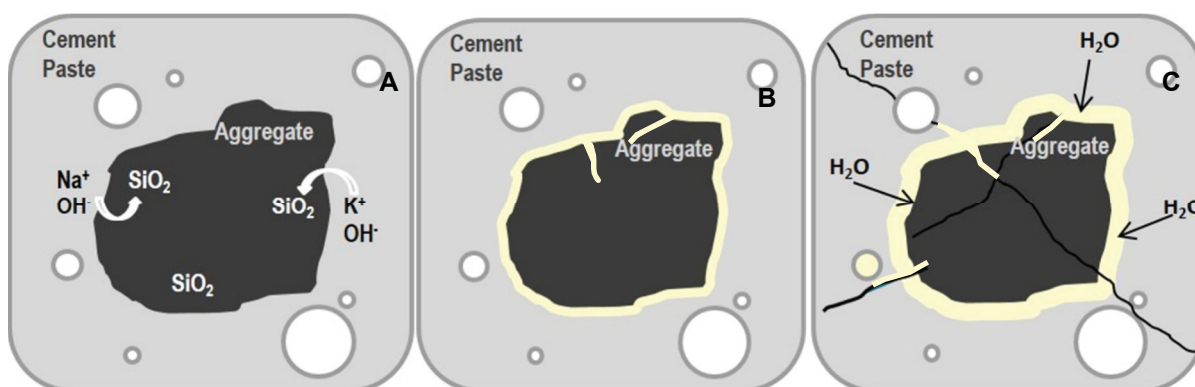
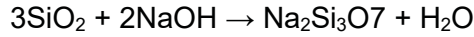
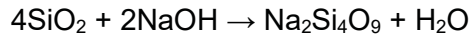


Figure 2.2. Simplified process of ASR (modified from Deschenes et al., 2009): A) alkali hydroxide ions reacting with reactive aggregates, B) expansive gel formed and C) cracking of the aggregate and cement paste.

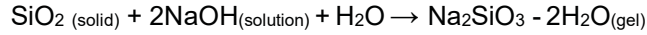
According to Poole (2017), the primary reaction occurs between the aggregate components and the alkali hydroxide solution in the cement paste pores.

Through the years several researchers have tried to express the reaction into different equations. Some examples are shown below:

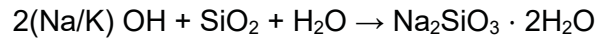
(1) Hansen (1944 in Poole, 2017) proposed the following idealized equations:



(2) French (1980) and West (1996)

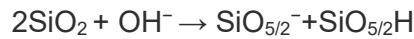


(3) Blight and Alexander (2011)

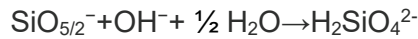


(4) Bulteel et al. (2004)

Step 1: acid-base neutralization reaction



Step 2: dissolution of silica forming silicate ions



Ca^{2+} plays an important role in ASR. Figueira et al. (2019) explained that Ca^{2+} reacts with dissolved silica forming the deleterious calcium-rich ASR gel rim around the aggregate particles. The authors also state that in the absence of Ca^{2+} , silica ions are dissolved and remain in the solution; also, as long as calcium is present in the pore solution, the dissolution of silica will continue. However, the role of $\text{Ca}(\text{OH})_2$ and Ca^{2+} is still the subject of debate.

The alkali-silica gel produced in this type of reaction is hygroscopic and the texture can vary from crystalline to amorphous (Fernandes, 2009). The chemical composition of gel is variable (Poole, 1992; Lindgård et al., 2012) and indefinite (Poole, 1992), being dependent on time (Lindgård et al., 2012) and its location in the concrete (Fernandes, 2009; Lindgård et al., 2012). A study conducted by Fernandes (2009) on concrete specimens extracted from different structures where mainly granite aggregates were used, led to the conclusion that the calcium was present inside the secondary ASR products, with higher content in the products located in cracks of the cement paste than inside the aggregate particle. The author also concluded that the expansion can occur even if the calcium is present or absent from the gel. Lindgård et al. (2012) concluded that the gel is composed of high but varying contents of silica, lower and varying contents of calcium and low and relatively constant contents of alkalis.

2.3.1. Reactive forms of silica in the aggregates

The presence of reactive forms of silica in concrete aggregates is one of the important factors for the reaction to occur. These forms of silica are the constituents of different types of rocks. In the literature, several rocks are considered potentially alkali-reactive. However, not all similar rock types are considered reactive; Lindgård et al. (2012) emphasize that they vary greatly due to their different geological history and geographical location. Also, Poole (2017) affirms that a certain rock type should not be synonymous with reactivity, and closer attention should be given to its constituents and texture instead of the rock type itself. Sims and Nixon (2003) even state that for several rock types, there are reactive and non-reactive varieties related to differences in the detailed mineralogical composition or texture. Lindgård et al. (2012) state that a given rock type can be considered innocuous in one country or region and reactive in another due to the different geological histories. The main deleterious constituents of aggregates are presented in Table 2.2.

The reactive silica phases in the aggregates are chemically unstable in the presence of a high pH (≥ 12.5) or dissolved alkali hydroxides (Deschenes et al., 2009) and tend to break down (Islam and Akhtar, 2013). Broekmans (2004) affirms that the dissolution of silica depends on pH and on the degree of crystallinity. Therefore, the alkali reactivity of aggregates is influenced by several factors (Islam and Akhtar, 2013; Figueira et al., 2019): chemical composition, geological history, texture and level of crystallinity. Other aspects that are taken into account in the reactivity of aggregates are the surface area, the microporosity and the particle size (Poole, 2017).

Stanton (1940) concluded that the particle size of the aggregates had an important impact on the expansion of mortars. One of the experiences conducted by Stanton is described by Thomas et al. (2013b); the author proved that the expansion of a reactive limestone was higher for mortars produced with the 180-600 μm fraction than for the larger fractions (0.6-2 mm and 2-6.7 mm), especially at earlier ages. This was attributed to the greater specific surface area and increased accessibility of the reactive silica. He also verified that the mortar bars produced with a reactive aggregate of particle size inferior to 180 μm did not exhibit any deleterious reaction. Also, Diamond and Thaulow (1974) tested opal aggregates within the range of 125–20 μm and found that the large expansions were detected for opal of all size fractions, even as fine as 30 μm – 20 μm . However, some contradictory results have been obtained by other authors. Zhang et al. (1999) showed that siliceous aggregates gave large expansions in the Chinese autoclave test for aggregate particle size within the range of 0.15–10 mm. Other studies demonstrated that some reactive aggregates when ground to filler size show a

pozzolanic reaction, which is considered beneficial for concrete inhibiting the reaction (Pedersen, 2004).

Table 2.2. Potentially alkali-reactive natural constituents in rocks / concrete aggregates (adapted from Kerr, 1977; Katayama and Kaneshige, 1986; Sims and Nixon, 2003; Blight and Alexander, 2011; Thomas et al., 2013b; Ramos, 2013; RILEM AAR-1.1, 2016).

Reactive constituents	Occurrence	Form	Chemical composition	Reactivity
Chalcedony	Commonly in chert/flint and limestone and in other lithologies	Commonly fine-grained fibrous microcrystalline to cryptocrystalline silica	SiO ₂	Generally attributed to its fine-grained nature and poor crystallinity
Cristobalite and trydimite	In some acid volcanic rocks, in some sandstones containing silicified fossils and in some flints.	Crystalline	SiO ₂	Metastable and quick to engage in deleterious ASR
Opal or Opaline Silica	Minor constituent in sedimentary rocks. It appears in cavities or seams of volcanic rocks	Microcrystalline to cryptocrystalline silica; commonly fibrous/poorly crystalline	SiO ₂ ·nH ₂ O	Usually highly alkali-reactive.
Quartz	Abundant in sands, gravels, many sandstones, and many light-coloured igneous and metamorphic rocks	Crystalline	SiO ₂	Some strained or micro- to crypto-crystalline silica may be potentially alkali-reactive.
Moganite	Frequently in chert, flint and in other lithologies altered at low temperature	Crystalline	SiO ₂	Very plausible contributor to deleterious ASR
Volcanic glass	Obsidian, pumice of felsic composition, or as a matrix in andesite, basalt, rhyolite, tuff, and other volcanic rocks	Amorphous	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , FeO, MgO, CaO, Na ₂ O, K ₂ O, H ₂ O, etc	Attributed to its amorphous, non-crystalline structure. Glass with SiO ₂ > 65 %
Devitrified glass	Matrix in andesite, basalt, rhyolite, tuff, and other volcanic rock types.	Amorphous to cryptocrystalline	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , FeO, MgO, CaO, Na ₂ O, K ₂ O, H ₂ O, etc	Prone to deleterious ASR. Tridymite or cristobalite might be present

Other aspects seem to influence the reactivity, like the permeability and porosity of the aggregates. For Broekmans (2002), porosity and/or microporosity in cherts merely enhances the chemical exchange with the outside world; it allows for reaction products to get out, but the effect is considered secondary and not fundamental. Lindgård et al. (2012) state that increased

permeability of aggregates with higher effective porosity may increase their alkali reactivity, because of the easy access to concrete pore fluids to reactive silica components.

Based on his research focusing on aggregates of circum-Pacific and Iceland, Katayama (1997b), divided reactive aggregates into three groups: (1) early expansive, (2) moderately expansive and (3) late expansive. The first group comprised opaline rocks (opaline shales and opalized volcanic rocks – rhyolite), andesite and dacite, rhyolite and obsidian. The second group integrated devitrified rhyolite, flint and chert, while the last group included sandstone, argillaceous rocks, slate and phyllite, impure limestone, metaquartzite and quartz schist. Ponce and Batic (2006) also grouped the aggregates according to their reaction rate: (1) rapid-reacting aggregates and (2) slow-reacting aggregates. Volcanic rocks containing volcanic glass and sedimentary rocks with opal and chalcedony are part of the first group. The second group is composed of granitic (magmatic rocks) and metamorphic rocks that contain quartz exhibiting deformation signs. Based on the results of laboratory tests and field performance of European aggregates, Lindgård et al. (2010) concluded that they can be classified into: (1) “normally” reactive (5 to 20 years), (2) slowly reactive (+15 to 20 years) and (3) non-reactive. The first group includes silicified limestone; greywacke; crushed gravel with silicified limestone and chert; gravel with limestone, chert and flint; cataclasite; gravel with quartzite and chert; gravel with opal, flint. The second group corresponds to sea gravel with semi-dense flint; gravel with quartzite and gneiss; sandstone; gravel with rhyolite and quartzite; gravel with sandstone, rhyolite and mylonite. The last group comprises the following combinations: gravel with flint; non-reactive limestone; gravel with quartzite, flint, greywacke and granitoid; gravel with meta-rhyolite and greywacke granitic sand; silicified limestone; dolomitic limestone; siliceous sand.

According to Lindgård et al. (2012) rocks with opal are examples of the fastest reactive aggregates, giving normally reliable results in the accelerated laboratory tests. On the other hand, aggregates containing quartz are considered more slowly reactive, affecting structures after a few decades (Leemann et al., 2015). Also, in RILEM AAR-7.1 (2016), the aggregates are separated into three levels of reactivity: (1) Low reactivity aggregates (aggregates identified as “non-reactive” in AAR-0); (2) Medium reactivity aggregates (e.g., siliceous sands and gravels) and (3) High reactivity aggregates (aggregates shown by tests using concrete specimens - AAR-3 - to have low alkali thresholds). In the same recommended specification, it is highlighted that aggregates with substantial proportions of opal are considered to be even more reactive than high reactivity aggregates and therefore should not be used in concrete or used with special precautions that are considered effective by trials.

Poole (2017) states that for a siliceous material to be alkali reactive, it must be poorly crystalline, should have defects or be amorphous or glassy in character. Figueira et al. (2019)

state that the attack by the hydroxyl and alkali ions penetrates deep into the interior of poorly crystallized silica, causing its dissolution, while it remains superficial in the case of well-crystallized silica forms.

For example, quartz and opal are both forms of silica with similar chemical composition but with differences in crystalline structure (Figure 2.3.). Opal is highly reactive while quartz is more stable (Thomas et al., 2013b).

Quartz can be found in a strained and/or deformed state, being considered thermodynamically unstable (Ponce and Batic, 2006). The reactivity of quartz seems to be related to defects in its crystalline structure, which make it unstable in contact with alkali hydroxides in concrete pore solution (Ponce and Batic, 2006) and thus facilitate its dissolution (Leemann et al., 2015). The amorphous nature of volcanic glass, with no ordered atomic structure and metastable (Best, 2003), makes it susceptible to being dissolved in an alkaline environment, thus causing ASR (Leemann et al., 2015). Also, chalcedony and opal, which are poorly crystalline forms of silica, react quickly with the alkaline pore solution of concrete (Katayama, 1997b; Leemann et al., 2015). Broekmans (2002) states that in the case of opal, which is composed of tightly packed micro-spherules of hydrated silica, the interstices between the opal spherules represent channels allowing dissolution all over the grain instead of being restricted to cracks or grain borders.

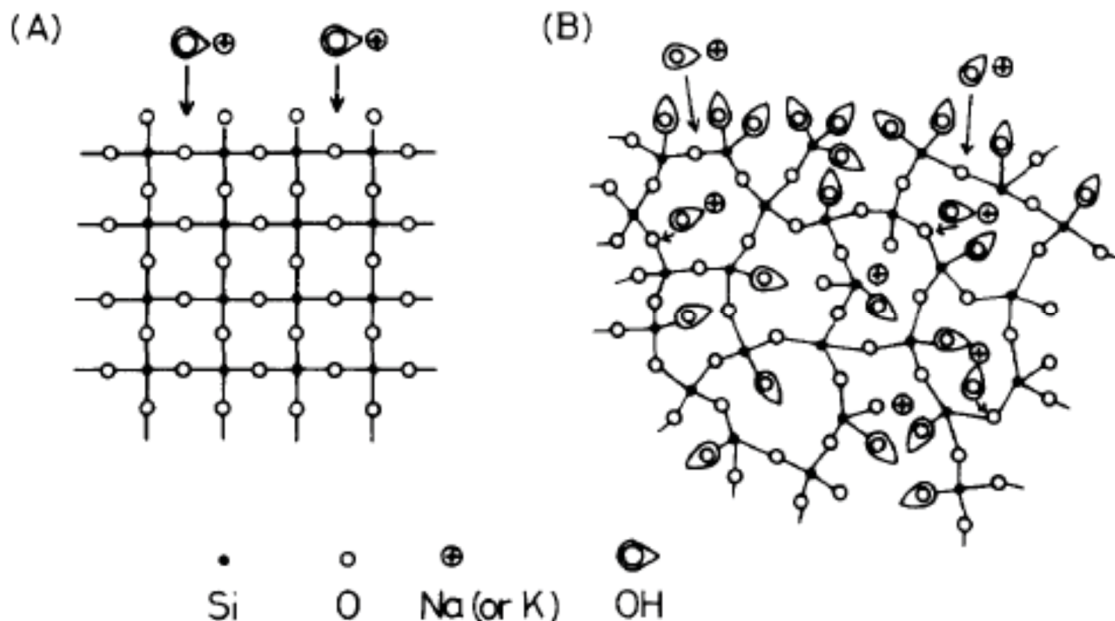


Figure 2.3. Differences in the crystalline structure of opal and quartz (Dent Glasser and Kataoka, 1981).

According to Rajabipour et al. (2015), the SiO_2 considered to be the most reactive is the amorphous SiO_2 (e.g., opal, natural or synthetic glass), followed by metastable forms such as cristobalite and tridymite, micro-crystalline silica, and other crystalline forms containing lattice defects, residual strains, or internal microcracks.

Beyond different findings of Stanton in his research on ASR, the researcher also showed that expansion does not necessarily increase with increasing reactive aggregate content (Thomas et al., 2013b). Stanton observed that for a fixed proportion of reactive aggregate, the expansion became the maximum at a certain grain size and that the expansion decreased when the particle size was increased or decreased from that size (Ichikawa, 2009). This phenomenon is known as “pessimum” behaviour (Hobbs, 1988; Sims and Nixon, 2003b), “pessimum” phenomenon (Katayama et al., 1996), or “pessimum” effect (Fournier and Bérubé, 2000; Thomas et al., 2013b; Nixon and Fournier, 2017). It consists of some aggregates having a maximum expansion for a given proportion and/or size fraction of a reactive particle (Fournier and Bérubé, 2000). Hobbs (1988) states that the proportion of reactive material contained in an aggregate leads to maximum expansion that corresponds to a peak expansion called the pessimum content. The author explained this phenomenon by dividing the expansion plot into four regions (Figure 2.4): (1) Region A – reactive silica content is low and gel growth is insufficient to produce cracks; (2) Region B - expansion continues until all the reactive silica is depleted; (3) Region C – the reaction continues but expansion ceases when alkalis are reduced; (4) Region D - reactive silica content is very high and the reaction is so rapid that the gel growth is too slow to crack the concrete.

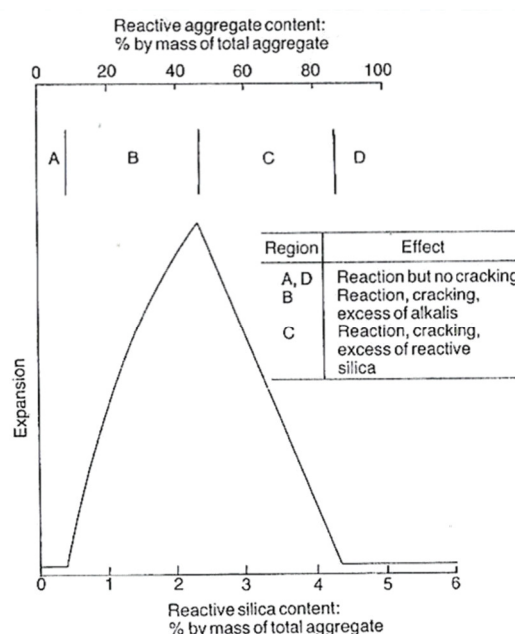


Figure 2.4. Pessimum behaviour; $w/c=0.4$ and $a/c= 2.75$ ratios, alkali content 6 kg/m^3 (Hobbs, 1988).

Opal is considered a highly reactive and early-expansive form of silica with a small pessimum proportion (Katayama et al., 1996), usually with values between 2% and 5% for pure opal (Brouard, 2012). The author also states that in the case of aggregates containing flint, expansion occurs with a flint content of 20% to 30% but the expansion does not occur anymore when it exceeds 60%. For volcanic glass, Katayama (1997b) affirms that it does not exhibit pessimum phenomena. Sims and Nixon (2003b) state that the presence of cryptocrystalline and microcrystalline quartz and chalcedony in chert causes slower expansion with larger pessimum proportions than reactive andesites in Japan. The “pessimum” contents of potentially alkali-reactive silica minerals and volcanic glasses are presented in Table 2.3.

According to Katayama (2012), the “pessimum” content of silica minerals generally increases with a decrease in the potential reactivity from opal to microcrystalline quartz.

Table 2.3. “Pessimum” proportions of silica minerals and volcanic glasses in mortar bars (adapted from Katayama, 1997b; Katayama et al., 2021).

Silica minerals/volcanic glasses		Pessimum proportion
Silica minerals	Opal	< 5 %
	Cristobalite	< 10 %
	Tridymite	< 10 %
	Chalcedony	20 %
	Cryptocrystalline silica	50 %
	Microcrystalline quartz	> 80 %
	Strained quartz	100%
Volcanic glasses	Rhyolitic glass	100 %
	Dacitic glass	100 %
	Andesitic glass	Marginal
	Basaltic glass	Innocuous

2.3.2. Presence of alkalis in concrete

The major source of alkalis comes from Portland cement which is commonly used for concrete manufacturing. The proportion of alkalis in cement depends on the composition of the raw materials (e.g., clay, limestone, chalk, shale and sometimes coal ash) used together with minor other components (Poole, 2017). Besides Portland cement, other sources that are

responsible for the contribution of alkalis to the pore solution include (Thomas et al., 2013b): supplementary cementing materials (e.g., fly ash, slag, silica fume, natural pozzolans); aggregates; chemical admixtures, external sources (e.g., seawater and deicing salts); wash water (when used).

The hydration of Portland cement produces an interstitial concrete pore solution composed mostly of dissolved calcium hydroxide ($\text{Ca}(\text{OH})_2$), potassium hydroxide (KOH) and sodium hydroxide (NaOH). The alkali compounds in the clinker are mainly: alkali sulphates (Na_2SO_4 – thenardite; K_2SO_4 – arcanite; $(\text{Na}, \text{K})_2\text{SO}_4$ – sodium and calcium sulphate; and $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ – calcium langbeinite) (Fernandes, 2005; Ramos, 2013); (ii) alkali aluminates, alkali aluminoferrites and alkali silicates (Hobbs, 1988).

The composition of the pore solution varies from the first contact between water and cement up until 28 days of the concrete placement. According to Thomas et al. (2013b), during the first few hours, the pore solution is mainly composed of alkali sulfates (Na^+ , K^+ , and SO_4^{2-}), but beyond that time, the formation of solid sulfate phases (calcium mono-sulfo-aluminate and ettringite) results in a reduction of the SO_4^{2-} concentration in solution. The hydroxyl ions (OH^-) then come into the solution to maintain balance with the positively charged alkali cations. Hobbs (1988) states that when cement is mixed with water, the alkali sulphates are converted into alkali hydroxides, which rises the hydroxyl concentration (and the pH) in the liquid phase. After the first day, the pore solution is composed mostly of Na^+ , K^+ , and OH^- (Thomas et al., 2013b); the alkali content will continue rising and at about 28 days most of the alkalis have gone into the solution (Hobbs, 1988). On the other hand, the pore solution is saturated with calcium (Ca^{2+}) but the concentration is very low (Thomas et al., 2013b).

The alkali content of cement is expressed by the equivalent sodium oxide ($\text{Na}_2\text{O}_{\text{eq}}$), with the following equation:

$$\% \text{Na}_2\text{O}_{\text{eq}} = \% \text{Na}_2\text{O} + 0.658 \% \text{K}_2\text{O}$$

The value of 0.658 is the result of the ratio of the atomic mass of Na_2O to K_2O

$$\frac{\text{Na}_2\text{O}}{\text{K}_2\text{O}} = \frac{(22.99 \times 2) + 16}{(39.10 \times 2) + 16} = 0.6579 \approx 0.658$$

Another equation is used for the calculation of the alkali content of concrete, where the equivalent alkali content of the cement is multiplied by the cement content of the mix plus other sources of alkalis used in the mix (Nixon and Sims, 2006; Nixon and Fournier, 2017):

$$\text{Concrete alkali (kg/m}^3\text{, Na}_2\text{O}_{\text{eq}}) = \text{cement alkalis (\%, Na}_2\text{O}_{\text{eq}}) \times \text{cement content (kg/m}^3) + \text{other sources of alkalis}$$

According to Hobbs (1988), the pH of concrete varies between 12.7 to 13.1 for a low-alkali content and between 13.5 to 13.9 for a high-alkali content, which means that, despite having a certain pH increase, the concentration of hydroxyl ions in concrete with a high alkali content will be ten times higher than that of concrete with a lower alkali content. Fernandes (2005) states that the increase in the concentration of hydroxyl ions in the solution enhances the attack on reactive aggregates, which indicates that the pore solution has high pH values. Also, the pH of the pore solution largely depends on the alkali content of the cement (Ramos, 2013).

One of the measures adopted to prevent ASR begins with the imposition of limits on the cement alkali content. Stanton in his work showed that the reaction did not occur when the cement alkali content was below 0.60% Na₂O_{eq}. (Thomas et al., 2017). Nowadays, this value appears in many specifications and is used as a reference for low alkali cement to be used for laboratory expansion tests (concrete prism test - ASTM C 1293, 2020) by the cement requirement specifications of the ASTM C 150 (2016).

Ramos (2013) states that the use of low-alkali cement has been effective when used in conjunction with slightly to moderately reactive aggregates. However, some research conducted over the years demonstrated that this value is not low enough to inhibit the ASR to occur with many aggregates (Farny and Kerkhoff, 2007; Thomas et al., 2013b; Ramos, 2013; Thomas et al., 2017). Figueira et al. (2019) reported that some studies revealed that ASR may develop with the cement of Na₂O_{eq} between 0.45% and 0.60% while other studies showed that cement with Na₂O_{eq} of 0.40% or less rarely induced reaction. Thomas et al. (2013b) affirm that the best approach is probably to limit the maximum alkali content of concrete.

Alkalis in concrete can come directly from the aggregates. Leemann et al. (2015) affirm that the alkalis present in reactive volcanic glasses, feldspars, micas, nepheline, clays and zeolites, especially when weathered, may be released into the concrete pore solution, thus contributing to ASR. Also, Fernandes et al. (2017) state that altered feldspars and mica are listed in the *Association Française de Normalisation* AFNOR FD P 18-543 (2014) as potential sources of releasable alkalis since they are considered as other forms of silica unstable in the alkaline environment of deformed rocks.

Sims et al. (2019) affirm that in several investigations, certain rock types in aggregate, like granite and some volcanic rocks, have been found to contain sufficient 'releasable alkalis' to

contribute to the development of ASR. Kawamura et al. (1989) found that the alkali-bearing reactive andesites responsible for the deterioration of concrete in Japan due to ASR leached relatively large amounts of alkalis up to at least 90 days of immersion in a saturated calcium hydroxide solution. Goguel (1995) used leaching techniques to investigate the release of alkalis from volcanic aggregates used in mortars. The author found that the alkali release during the first six months was about 1% $\text{Na}_2\text{O}_{\text{eq}}$ for a rapidly cooled fresh basalt with poorly crystallized feldspars and about 0.1% for a well-crystallized basalt. He concluded that the release of alkalis was not attributed to the simple presence of a particular mineral (e.g., plagioclase) but rather to the different cooling histories of the basalts tested. The particle size effects of the glass phase and the structural strain, especially in the plagioclase crystals, are some of the parameters that are related to the cooling history of each rock.

So far, there is not a widely accepted method for assessing the potentially releasable alkali content of aggregates. The most recent proposal was published by Menéndez et al. (2021) as the AAR-8 method (for assessing the additional reactive alkalis that can be leached from aggregates) after a draft discussed in Nixon and Fournier (2017). The RILEM AAR-7.1 (2016) recommends that this source of alkalis should not be included in the concrete alkali content calculations, except in the case of concrete in S3 structures (e.g., nuclear installations, dams, tunnels). In such structures, the possibility of alkali release by aggregates containing significant amounts of altered and/or weathered feldspar, or other minerals capable of releasing alkalis, should be considered.

Hobbs (1988) reported that external sources of alkalis, such as deicing chemicals, may increase the hydroxyl ion concentration in the pore solution and consequently the risk of ASR. Freitag et al. (2003) also suggest that the use of sodium chloride in deicing salts may increase alkali concentrations. Katayama et al. (2004) studied concrete cores from different highway bridges in the Hokuriku district in Japan influenced by deicing salts. The authors showed that both the aggregates and the deicing salts contributed to increasing the water-soluble alkali content of the concrete towards reaching the threshold value required to produce ASR. The RILEM AAR-7.1 (2016) recommendation mentions that there is good evidence that the use of sodium chloride-based deicing salts can aggravate ASR. It also states that in the USA, there is recent evidence that deicing products with sodium or potassium formates and acetates can cause ASR-like damage to concrete, even when concrete comprises non-reactive aggregates. Also, Lindgård et al. (2017) reported that the ASR damage observed in many bridges (the 1960s and 1970s) in Denmark is linked to the use of deicing salts, which is responsible for the increase in alkali content. RILEM AAR-7.1 (2016) recommendation state that it is not possible to quantify the alkalis provided by deicing salts to enter the calculation of the alkalis in the

concrete. Instead, it is suggested to take into account the environmental class E3 of concrete that corresponds to structures exposed to extraneous moisture plus aggravating factors.

Regarding the chemical admixtures, Lindgård et al. (2012) state that they can only influence ASR if it contains significant quantities of sodium, potassium and lithium, emphasizing that the new generations of admixtures generally do not contain alkalis.

2.3.3. Moisture

The presence of water is one of the main factors for the development of ASR. Some concrete structures are more susceptible to expansion; these are: highway pavements and bridges, parking garages, and water-retaining and underwater structures (ACI 1998). Also, Poole (1992) indicates that the parts of a concrete structure that are more severely cracked and damaged by ASR are those that are more exposed to the elements.

Water seems to play two roles in the case of ASR (Poole, 1992; Ramos, 2013; Poole, 2017): (1) as a transport agent for ions in the pore solution and (2) as an essential element for gel swelling to take place. This means that water is a vehicle for transporting the alkali ions to the reaction sites where the gel absorbs water, thus leading to expansion (Farny and Kerkhoff, 2007) and cracking.

Lindgård et al. (2012) indicate that the water content in concrete structures is usually referred to as relative humidity (RH), which is a measure of the thermodynamic state of the pore water. Fournier and Bérubé (1993) and Larive et al. (2000) affirm that the critical limit for the ASR to develop is within the range of 80-85% RH or 80-90% RH, respectively. Stark (1990) also affirms that RH of at least 80% to a temperature of 21 to 24°C is required in concrete for maintaining ASR expansion. Poole (1992) reported that the effects of ASR expansion vary directly with the percentage of RH in the concrete. This is demonstrated in Figure 2.5 where the expansion is considered negligible for RH=70%, whilst it increases significantly for RH above 80%. It is generally recognized that ASR ceases below an RH of about 80% (ACI 1998; Fournier et al., 2010; Thomas et al., 2013b); however, if the reaction has already occurred, water contribution will lead to quick expansion (Larive, 1997). RH will usually remain at or above 80% just beneath its surface (Poole, 1992), even in arid regions (Stark 1990), and this for several decades (Farny and Kerkhoff, 2007).

Lindgård et al. (2012) indicate that it is not easy to reliably and accurately measure RH, especially in the field. Reed et al. (2016) state that the existing procedures for measuring RH: (1) are time-consuming; (2) require several hours of equilibration time and (3) require specific

external conditions to yield accurate results. One of the problems reported by the authors is the fluctuation in temperature in the field; good results are obtained when the temperature of the concrete ranges between 21 to 24°C.

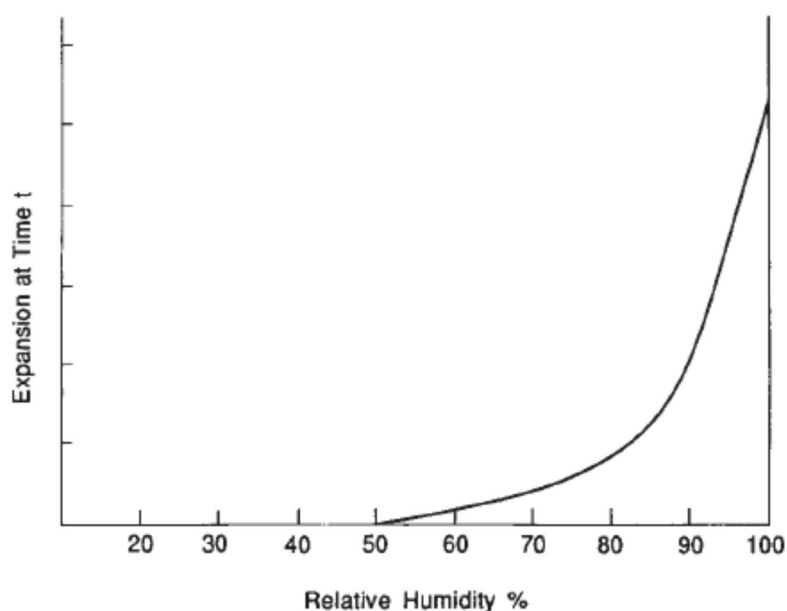


Figure 2.5. The effect of relative humidity on the expansion of concrete due to ASR (Poole, 1992).

A study performed by Ólafsson (1986) showed that temperature affects RH and consequently mortar bar expansion; the author found that RH might decrease with the rise of temperature, being around RH=70% at 38°C.

Another factor that can reduce ASR expansion is related to permeability and water-cement ratio. According to Farny and Kerkhoff (2007), any reduction in permeability, due to the use of a low water-to-cement ratio, supplementary cementitious materials (SCMs), or other means, reduces the movement of moisture and alkalis into and within the concrete. This statement is in agreement with ACI (1998). However, the authors emphasize that concrete with a lower water content will contain a higher alkali concentration in the concrete pore solution.

Figueira et al. (2019) assume that concrete structures are generally susceptible to ASR, except those where the internal humidity is maintained/controlled to values lower than 80% and those permanently protected from atmospheric conditions and other sources of moisture.

2.4. Diagnosis

In general, deterioration is a consequence of the joint action of internal and external factors (Ferreira, 2000), and is rarely attributed to a single cause (Neville, 2011). According to Fournier et al. (2010), in regions where there are freezing and thawing cycles, the damage to concrete can be enhanced when the concrete is already affected by ASR, sulphate attack or other deleterious mechanisms.

The visible damage caused by ASR normally takes time and does not appear in the first five years of a concrete structure, unless it contains highly reactive aggregates or other mechanisms are deteriorating the structure rather than ASR (Godart and De Rooij, 2017).

ASR is considered to be one of the various mechanisms that might be fully or partly contributing to the deterioration and premature loss in serviceability of concrete structures (Fournier et al., 2010; Thomas et al., 2013b). Farny and Kerkhoff (2007) conclude that the presence of reaction products does not indicate that destructive ASR is happening; on the other hand, harmful ASR does not occur without the presence of secondary reaction products. The authors state that a cause-and-effect relationship must connect the occurrence of reaction products to harmful ASR. Also, Fernandes and Broekmans (2013) refer that the presence of alkali-silica gel on the surface of the concrete is indicative of ASR, but it does not mean that the reaction is deleterious. Godart and De Rooij (2017) affirm that many concretes can show very localized areas with ASR gel but that the proportion of reactive particles may not be sufficient to produce cracking or damage to the structure.

Several procedures have been proposed and followed to evaluate the cause of concrete deterioration. For ASR to be confirmed in a deteriorated concrete structure, an extensive field and laboratory testing program must be followed (Fournier et al., 2010). But, in a routine site inspection, all forms of deterioration should be taken into consideration. Some of the procedures for diagnosing ASR are described in BCA (1992), Fournier et al. (2010), Blight and Alexander (2011), Thomas et al. (2013b), and Godart et al. (2013) (Table 2.4).

It is important to use the appropriate investigation tools for the diagnosis of ASR in a concrete structure. Fournier et al. (2010) describe different investigation tools/tests for the diagnosis of ASR: site investigation, documentary evidence on concrete structures investigated, initial and periodic measurement of cracks (Cracking Index Method), petrographic examination (macroscopic and microscopic examination), mechanical testing (Stiffness Damage Test).

Table 2.4. Procedures for the diagnosis of ASR according to different authors.

Authors	Procedures for the diagnosis of ASR
BCA (1992)	1) site inspection and testing; 2) sampling; 3) laboratory investigation; 4) assessment; 5) risk of future reaction.
Fournier et al. (2010)	<i>Level 1</i> - condition survey; <i>Level 2</i> - preliminary studies for the diagnosis of ASR (cracking index method, preliminary sampling program and petrographic examination on polished and thin sections); <i>Level 3</i> - detailed studies for the diagnosis/ prognosis of ASR (detailed laboratory investigations).
Blight and Alexander (2011)	1) Desk study of existing records and information; 2) Field inspection of structure; 3) Evaluation of field inspections results; 4) Sampling of concrete; 5) Visual examination of cores aided by stereomicroscope; 6) Proceed with Testing; 7) Write a diagnostic report.
Thomas et al. (2013b)	<i>Step 1</i> – diagnosis (condition survey, documentation, sampling of structural components, diagnosis - petrographic examination, conclusions) <i>Step 2</i> – prognosis (in-situ investigations, advanced laboratory investigations – DRI, mechanical testing and alkali content of concrete - collective assessment of in-situ and laboratory investigations)
Godart et al. (2013) (RILEM AAR-6.1)	1) Strategy (background information about the concrete structure); 2) on-site (field inspection of the structure and coring of samples); 3) laboratory (visual examination of the cores, petrographic examination, additional tests); 4) reporting (interpretation and report writing).

2.4.1. Visual symptoms of ASR

A routine inspection is considered to be the starting point of a cyclic process to maintain the safety and reliability of a concrete structure (Godart et al., 2013, Godart and De Rooij 2017).

The visual symptoms of ASR are usually detected during a routine inspection (Godart and De Rooij, 2017). These generally include the following: (1) cracking, (2) movements, displacements and deformations, (3) surface deposits (exudations v.s. efflorescence) and (4) pop-outs. Despite all of those symptoms occurring when ASR is present, they are not exclusively indicative of this type of deterioration (Fournier et al., 2010).

Some of the visual symptoms of concrete deterioration caused by ASR (e.g., cracking) can also be associated with other pathologies (e.g., drying shrinkage, thermal contraction, frost attack, sulphate attack, corrosion of the reinforcing as a result of chloride ingress) (BCA, 1992; Blight and Alexander, 2011), and even between ASR and ACR (e.g., evidence of expansion, relative movements between structural members showing different expansion rates, cracking) (Fournier et al., 2010), which makes it harder to draw conclusions based on in-situ observations only.

Cracking

Cracks appear in concrete structures for many reasons and may not have only a single cause (BCA, 1992). They are the most common feature of ASR (Poole, 1992). Usually, they do not affect by themselves the structural integrity although they may be an indication of some (serious) issues affecting the structure. Most often, they turn out to be facilitators by allowing the access of weathering factors to the interior of concrete (Fernandes and Broekmans, 2013) accelerating damage development (BCA, 1992). Cracking generation is influenced by: (1) the shape or geometry of the concrete member, (2) the environmental conditions, (3) the presence and arrangement of reinforcement, and (4) the load or stress fields applied to the concrete (Fournier et al., 2010). There are some distinct differences in the crack pattern affecting non-reinforced and reinforced concrete members. In the case of concrete elements without reinforcement, the cracks generally appear in a random pattern (commonly called *map or pattern cracking*); however, reinforced concrete structures (RCS) will show cracking in directions matching the underlying rebar network (Figueira et al., 2019) (Figures 2.6A, 2.6B, 2.7A, 2.7B and 2.7C).

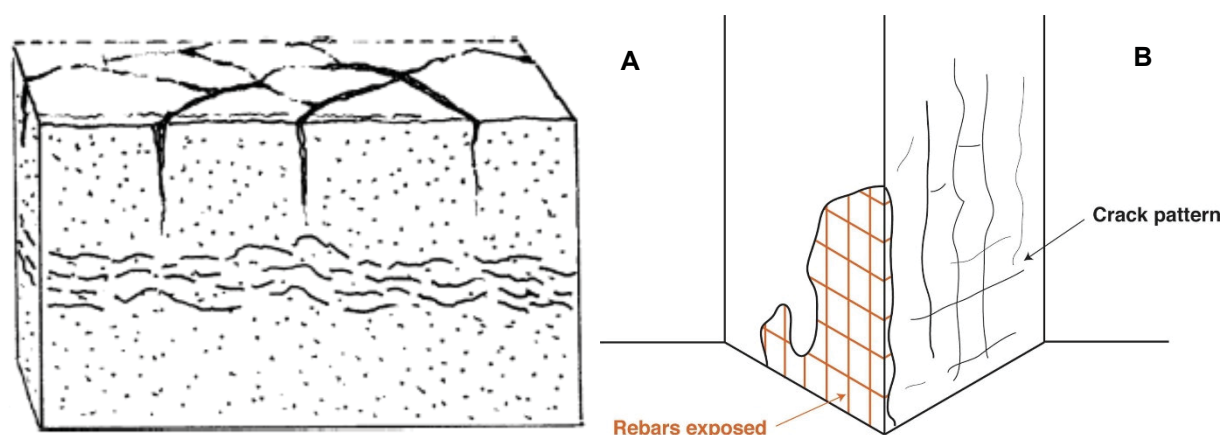


Figure 2.6. Schematic representation of ASR cracking: (A) map-cracking (ACI 1998) and (B) in one or two directions in RCS (Figueira et al., 2019).

Humidity plays an important role in the development of cracks. Hobbs (1988) affirms that cracking occurs preferentially in concrete exposed to rain or heavy condensation, while Fournier et al. (2010) report that cracking is more severe in areas where there is a constant supply of moisture.

Another important aspect taken into consideration is the width of the cracks. Fine cracking (width < 0.1 mm) is present in almost all concretes, and the cause is attributed to surface drying and shrinkage, among other causes; however, cracks with widths higher than 0.5 mm may be an indication of some structural issues and should often be monitored and considered for further investigations (Godart et al., 2013). Fournier et al. (2010) point out that the measurements of cracks widths can be used to know/monitor the development of damage between different members of a structure; it is also common practice to measure crack widths as part of routine visual condition surveys, thus allowing to monitor progress in damage. Table 2.5 shows a classification of in-situ crack widths according to Godart et al. (2013). It is an initial guideline to assess the severity of cracking.



Figure 2.7. Patterns of cracking in concrete due to ASR: (A) map-cracking in concrete pavement, (B) Map cracking in the wing wall of a highway bridge structure, and (C) longitudinal cracking following the main reinforcement in columns of a highway concrete structure (with compliments of B. Fournier).

Table 2.5. Classification of the cracks based on their width on site according to Godart et al. (2013).

Cracks width (mm)	Description		Abbreviation
< 0.1	Fine	Usually present	F
0.1 – 0.3	Normal	Normal limit for RC	N
0.3 – 0.5	Large	Over limit	L
0.5 – 1.0	Moderately wide	Record all	MW
2.0 – 5.0	Wide	Refer to Engineer	W
>5.0 – 10.0	Very wide	Refer to Engineer	VW

Movements, displacements and deformations

A concrete structure can suffer from movements, displacements and deformations as a result of different causes including expansion due to ASR (Figure 2.8). According to Fournier et al. (2010), the development of ASR in a concrete structure is not homogeneously distributed, varying between or within different parts of the structure as a function of various factors such as: (1) differences in the proportioning and composition of concrete (e.g., concrete obtained by different suppliers and with aggregates containing different reactivity levels, cement of different alkali contents); (2) variations in the exposure conditions and loading regimes between and within the various parts of the structure; (3) differences in the size and geometry of different parts of the structures, (4) variations in the reaction rates between different parts of the structure (due to leaching, dilution, deicing salts, etc.); (5) variations in the structural restraints within and between the different parts of the structure; (6) variations in the age of the different structural members (e.g. structure built in different stages). For example, differential expansion/movement between structural concrete members affected at different rates by ASR can cause a malfunction of the spillway gates in dams, where the operation of machinery can be significantly compromised (ACI, 1998; Fernandes and Broekmans, 2013).



Figure 2.8. Misalignment in the crest of a concrete dam due to ASR (Fernandes and Broekmans 2013).

Surface discolouration (gel exudations vs. efflorescence)

The surface discolouration occurs usually in combination with cracking (Poole, 1992; Farny and Kerkhoff, 2007) by bordering them in ASR-affected concrete members (BCA, 1992; Fernandes and Broekmans, 2013). Poole (1992) states that the discolouration in this type of deterioration is probably due to the strong alkaline solutions that infiltrate along the cracks. In the case of fine cracks, they are marked by a dark discolouration giving the appearance of permanent dampness (BCA, 1992; Fernandes and Broekmans, 2013) (see Figure 2.9). Patchy surface discolouration may appear in areas where concrete is severely affected by ASR (BCA, 1992). Also, reacted particles sometimes display dark waxy rims either inside the particle or along the edges of the particles (Fernandes and Broekmans, 2013).

The surface deposits include efflorescence (Figure 2.10A) and gel exudations (Figure 2.10B). Although surface gel exudations are a common and characteristic feature of ASR (Fournier et al., 2010; Thomas et al., 2011), Poole and Sims (2016) consider that exudations of alkali-silica gel are not that common. For ASR gel to be present: (1) there has to be sufficient moisture available to transport the gel through the surface and (2) it has to be in locations protected from exposure to water, because the gel is soluble in water, (for the ones containing salts of sodium, potassium and sulphate ions), where most of the times are washed away from the surface of concrete due to rain.

The exudations are observed along cracks and in voids present in concrete. The gel that is exuded is generally white due to the carbonation of the originally transparent gel in contact with air.

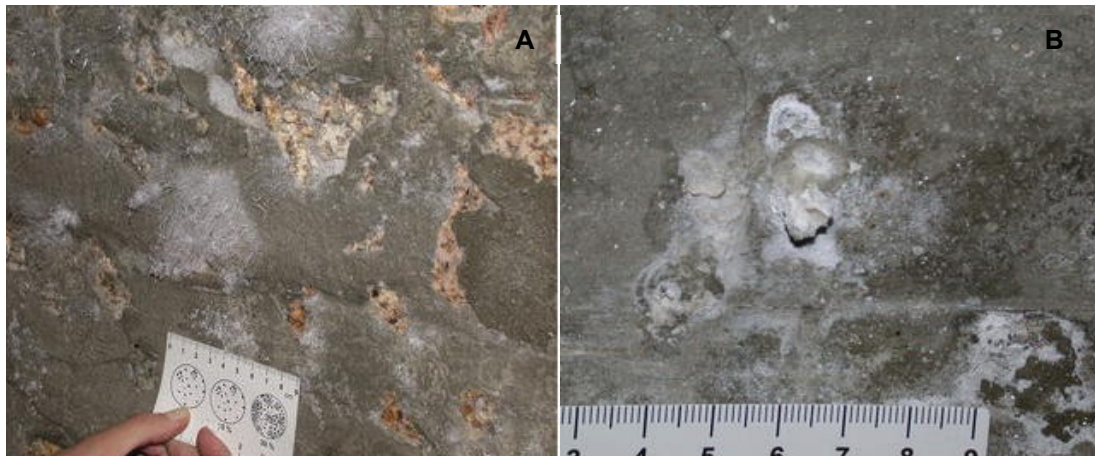


Figure 2.9. Interior wall in two different dams: (A) efflorescence and (B) gel exudation (Fernandes and Broekmans 2013).

Pop-outs

Pop-outs are also one of the features of ASR, although they are more frequently associated with freezing and thawing action (Thomas et al., 2011). In the case of ASR, pop-out occurs as the result of the expansion of individual reactive aggregate particles, thus forming a hole on the surface of the concrete member and leaving the particle exposed (Figure 2.10). The presence of alkali-silica gel in the pop-out is indicative of ASR (Fernandes and Broekmans, 2013; Owsiak et al., 2015; Poole and Sims, 2016).



Figure 2.10. Example of pop-out in a concrete element (Ramos, 2013).

The appearance of a pop-out begins with a semi-circular crack and with a vertical displacement of the semi-circular margin. As it progresses, the crack becomes approximately

circular and an inverted cone of material gradually stands out near the surface until a crater is formed with fragments of the expansive aggregate (Poole and Sims, 2016).

According to Farny and Kerkhoff (2007), pop-outs have been found in floor coverings, especially on slabs placed over wet cohesive soils with poor insulation. Owsiak et al. (2015) explain that humidity increases within concrete due to capillarity action, which may induce ASR. The same authors mention that pop-outs were observed on a concrete floor of an underground garage. Also, several pop-outs were found on an industrial floor in Italy (Baronio and Berra, 1989).

Normally, pop-outs do not affect the serviceability or the durability of concrete, causing only some surface degradations (Poole and Sims, 2016); it is thus generally considered a cosmetic issue (Farny and Kerkhoff, 2007; Fernandes and Broekmans, 2013).

Table 2.6 presents a summary of the different symptoms of deterioration that can be observed during site investigations. In this table, information is provided regarding the manifestation, preferential location and causes of deterioration.

Table 2.6. Signs of ASR, appearance, preferential location and causes.

Signs of ASR	Manifestation	Locations	Causes
Cracking (Hobbs, 1998; BCA, 1992; Fournier et al., 2010; Thomas et al., 2011; Fernandes and Broekmans, 2013)	<i>Map-cracking</i> Randomly-oriented cracks on the surface of concrete, form a network of fine cracks joined up in polygonal shapes and confined by larger cracks similar to limits in a map. Frequently observed in ASR-affected concrete free of major stresses or restraint.	<i>Preferentially:</i> - close to the waterline in piers, - in retaining walls, - in pavement slabs, - by wick action in piers or columns	Swelling from the uptake of water by ASR gel
	<i>Longitudinal crack</i> One or more directions with preference alignment usually are orientated in the same direction as the confining stresses. Usually observed in reinforced concrete.		<i>Others</i> - plastic shrinkage, - drying shrinkage, - early-age thermal contraction, - frost attack, - corrosion of steel reinforcement, - loading - sulphate attack
Movements, displacements and deformations (BCA, 1992; Thomas et al., 2011; Fernandes and Broekmans, 2013)	- misalignment, - distortion, - excessive deflection - separation of adjacent concrete members or structural units, - closure of joints causing extrusion of jointing and sealing materials,	Between and within concrete members/sections/parts, structural units	ASR: uneven or differential concrete swelling <i>Others</i> - Loading, - uniform or differential shrinkage,

Signs of ASR	Manifestation	Locations	Causes
Ramos, 2013)	- spalling of concrete at expansion or construction joints		-thermal or moisture movements, - gravity effects, - creep, -impact or vibration
Surface discoloration (Farny and Kerkhoff, 2007; Thomas et al., 2011; Fernandes and Broekmans, 2013; Ramos, 2013)	Cracks can show discolouration bleached, pinkish or brownish margins can extend up to several millimetres on each side of the crack, giving the appearance of permanent dampness	Along cracks	ASR: gel exudation in the vicinity of the cracks <i>Others</i> - leaching, - algae growth, - reinforcement corrosion ('rust')
Surface deposits (Gel exudations v.s. efflorescence) (Fournier et al., 2010; Thomas et al., 2011; Ramos, 2013)	<i>Gel exudations</i> Surface deposits of ASR gel are sometimes observed along cracks and voids in concrete. The gel colour is usually white with a jelly-like texture. <i>Efflorescence</i> Sugary deposits of mineral salts varying from calcium carbonate, sulphides, sulphates, chlorides and other salts of calcium and sodium calcium carbonate ranging in colour from white to dark grey	In the vicinity of the cracks	ASR: moisture movement through pores and cracks in concrete which transports the ASR gel to the surface, where it exudes <i>Others</i> - frost action - movement of water through cracked concrete members - leaching of salts
Pop-outs (Farny and Kerkhoff, 2007; Thomas et al., 2011; Poole and Sims, 2016)	Small conical-shaped cavity where the cement paste was detached leaving the reactive aggregate exposed. It may vary in size, but is commonly 25 mm to 50 mm; it can be smaller.	<i>Preferentially:</i> - Floor coverings at later ages, - slabs placed over wet cohesive soils.	ASR occurs to relieve pressure created by gel formed just beneath the concrete surface <i>Others</i> - Commonly forms because of the expansion and contraction of porous aggregate during freezing and thawing cycles. - poor bond between the cement paste and dusty coarse aggregate particles - a contaminant, corroding reinforcement

2.4.2. Laboratory investigations

The main objective of the laboratory investigations may include the *diagnosis* and the *prognosis* of a deteriorated structure (BCA, 1992). The samples that are cored from different parts of a concrete structure affected by ASR or other types of pathologies are subjected to several tests. According to Fournier et al. (2010), a detailed laboratory investigation includes, among others: sampling and treatment of samples, detailed petrographic examination (including DRI), mechanical testing (compressive and tensile strengths, elasticity modulus, stiffness damage test - SDT) and expansion tests on cores.

Preliminary examination of the samples in the laboratory

Immediately after extraction, cores must be wiped off to remove excess moisture and then wrapped in cling film to prevent drying (BCA, 1992, Fournier et al., 2010). Subsequently, they should be weighted and a macroscopic examination should be performed with the help of a magnifying lens (7x to 10x) and/or a stereo-binocular microscope (up to 60x) (Godart and De Rooij, 2017). All the cores should be photographed with a scale bar and in colour, with special attention being given to relevant features like cracking, reaction rims, presence of secondary deposits in voids and pop-outs (BCA, 1992). It is important to have a complete record and description of cores, including the diameter, overall length, place of origin, the composition and uniformity of the concrete, the aggregate types and sizes and the proportion of voids (BCA, 1992).

Petrographic examination

The identification of macroscopic features of deterioration on broken or polished surfaces of the cores is relevant in the diagnosis of ASR, some of these features are (Godart and De Rooij, 2017): (a) damp or “sweaty” patches - dark areas around any reacted aggregate particles; (b) reaction/weathering rims - dark outer/white inner rims around aggregate particles; (c) crack patterns of cement paste and internal cracking of aggregate particles; (d) presence of any ASR-gel – around aggregate particles, inside the particles, in the cement paste or exuding from the core; (e) the pattern/distribution of the above macroscopic features; (f) any other signs of irregularities. The identification of these features is important for selecting pieces of concrete for the preparation of thin sections (BCA, 1992). The areas showing the more pronounced features of deterioration and generally those selected for the examination, although care should be exercised in selecting specimens representative of the concrete condition (Godart and De Rooij, 2017).

Internal cracking can be observed during the examination of sawn and finely ground sections of concrete cores. Cracking can be present not only in concrete affected by ASR but also by other pathologies or processes, such as plastic shrinkage, thermal contraction, drying shrinkage, aggregate expansion and contraction, sulfate attack, frost attack and steel corrosion (BCA, 1992). In the report of BCA (1992), different cracking patterns that relate to major concrete pathologies are illustrated; the difference in the crack pattern of concrete incorporating a reactive fine aggregate and a reactive coarse aggregate is also highlighted (Figure 2.11.).

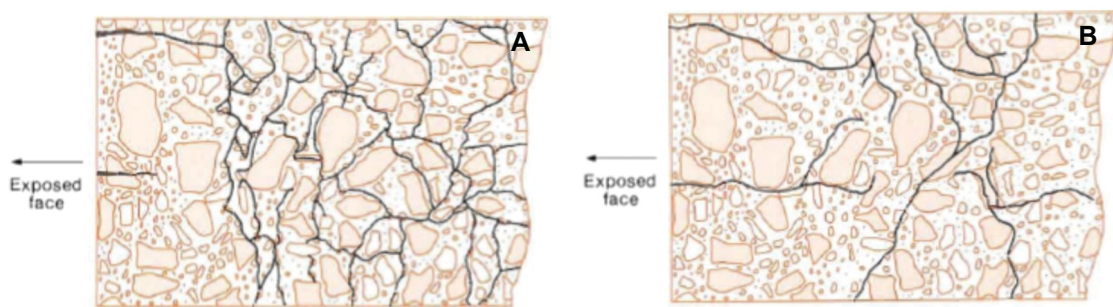


Figure 2.11. Internal cracking pattern caused by ASR: (A) reactive silica in the sand fraction and (B) reactive silica in the coarse aggregate (BCA, 1992).

The petrographic examination of thin sections will identify positively most of the diagnostic features of ASR (Godart and De Rooij, 2017). An experienced petrographer will recognize reactive and reacted aggregates and will confirm the presence of gel and cracking (BCA, 1992) by using a polarizing light microscope.

Petrographic examination of concrete will also allow identifying reactive rock types in the aggregate particles, the presence of cracks and ASR gel (Godart and De Rooij, 2017).

Some additional tests might be considered, such as the scanning electron microscope (SEM/EDS), which is used to confirm the presence and composition of secondary products from ASR or other pathologies.

Based on Ramos (2013) and Poole and Sims (2016), Table 2.7. relates the methods of examination and the different features observed through each method.

Table 2.7. Methods of examination and the different features observed based on Ramos (2013) and Poole and Sims (2016).

Methods of examination	Features
Observations on cores and polished slices	- white/darker reaction rims on reacted aggregate particles - gel deposits in air voids, cracks and broken faces and on the curved outer faces of cores, sometimes showing as damp or “sweaty” patches - cracking from the surface and into the concrete - internal cracking in reacted aggregate particles - cracking in the cement paste
Microscopic examination of thin-section (petrographic microscope)	- alkali-silica gel (typical colourless, usually conchoidally cracked) - reacted aggregate particles - cracking
Microscopic examination of thin-section and fragments(SEM)	- Alkali-silica gel: the appearance of the gel varies depending on its composition and where it occurs. It can appear foliated to massive or spongy and have a grainy texture. - Alkali-silica gel always contains silicon plus varying combinations and concentrations of calcium, potassium, and sodium

2.5. Preventive measures

Most of the preventive measures used to avoid ASR are related to the conditions in which the reaction occurred in the first place (e.g., a sufficient quantity of reactive silica in the aggregates, high alkali content in cement and high humidity), and it is recommended to avoid or limit the use of reactive aggregates and to minimize as much as possible the amount of alkalis in concrete (Thomas et al., 2013b). Other measures are also used in the combat of ASR, such as the use of supplementary cementitious materials (SCMs) and lithium-based compounds.

2.5.1. Limiting moisture

The concrete structures that are exposed to the environment or that are in contact with the ground normally have enough internal moisture to start ASR (Stark, 1991).

Regarding the external moisture, this depends on the environment to which the concrete structures are exposed. According to AAR-7.1 (2016), there are three categories of environmental classes relating to ASR development (Table 2.8), which are:

- E1. The concrete is essentially protected from extraneous moisture;
- E2. The concrete is exposed to extraneous moisture;
- E3. The concrete is exposed to extraneous moisture and additionally to aggravating factors, such as sodium chloride-based de-icing salts, freezing and thawing, or wetting and drying cycles in a marine environment.

According to the recommendations in RILEM AAR-7.1 (2016), there are four different precautionary measures, from which M3 is the one related to moisture: “Measures to reduce the access of moisture and maintain the concrete in a sufficiently dry state”. External cladding or tanking can be used to prevent additional moisture in concrete (AAR-7.1 2016); however, before using this type of measure, it should be taken into account that the presence of moisture within the concrete may be enough for ASR to remain active (Fournier et al., 2010). Furthermore, AAR-7.1 (2016) alerts that the use of cladding on a concrete structure may not be sufficient to reduce the moisture content in the air behind the cladding, especially in a cold and very humid environment; the use of cladding could thus be considered more viable for a warm and dry environment. Also, the inclusion of a well-designed drainage system that allows inspections and maintenance is highly recommended.

Table 2.8. Environmental classes (AAR-7.1, 2016).

Environmental class	Description	Environment of concrete
E1	Dry environment protected from extraneous moisture	• Internal concrete within buildings in dry (1) service conditions.
E2	Exposed to extraneous moisture	• Internal concrete in buildings where humidity is high; e.g., laundries, tanks, swimming pools • Concrete exposed to moisture from the external atmosphere to the non-aggressive ground or immersed in water. • Internal mass concrete should be included in this category (2).
E3	Exposed to extraneous moisture plus aggravating factors	• Internal or external concrete exposed to de-icing salts. • Concrete exposed to wetting and drying cycles by seawater (3) or salt spray. • Concrete exposed to freezing and thawing cycles whilst wet. • Concrete subjected to prolonged elevated temperatures whilst wet. • Concrete roads are subjected to fluctuating loads.

(1) A dry environment corresponds to an ambient average relative humidity condition lower than 75 % (normally only found inside buildings) and no exposure to external moisture sources.
(2) A risk of alkali-silica reaction exists for mass concrete elements in a dry environment because the internal concrete may still have high relative humidity. Vulnerable mass concrete elements are those with the least dimension of 1 m or more.
(3) Concrete constantly immersed in seawater does not suffer a higher risk of ASR than a similar element exposed to humid air, buried in the ground, or immersed in pure water, because the alkali concentration of seawater is lower than the alkali concentration of the pore solution of most concretes, and the penetration of chloride ions is usually limited to a few centimetres.

The application of a coating or sealer is another method mentioned by Fournier et al. (2010) and RILEM AAR-7.1 (2016) for limiting moisture. This works like a barrier preventing external

water to enter the concrete and at the same time permits water vapour from within the concrete to exit, thus causing an overall decrease in the internal relative humidity. Siloxanes and silanes are the most common sealers used for preventing/controlling ASR; they are also used to reduce the entrance of water to promote frost resistance and reduce the rate of corrosion of reinforcing steel from external chlorides (Fournier et al., 2010). Deschenes et al. (2016) studied a concrete pavement in Arkansas where silane treatment was selected to mitigate ASR. The authors concluded that the majority of the silane-treated sections have suffered a slow progression of expansion, although they emphasize that more time is required to fully assess the efficacy of silanes. The RILEM AAR-7.1 (2016) affirms that the effectiveness of this kind of surface treatment (coatings and impregnations) have been found to vary because this is generally not considered a sufficient precautionary measure in preventing ASR.

One of the notes from AAR-7.1 (2016) affirms that the efficacy of precautionary measure M3 is difficult to guarantee, especially in wetter climates, and it is not recommended as the only precautionary measure in S3 (high-risk) structures.

2.5.2. The use of non-reactive aggregates

Normally, the sources of aggregates that are used in concrete are not far from the areas of demand. This is due to the large tonnage of aggregates used in concrete and the high cost of transportation (Alexander and Mindess, 2005). However, the limitation of using reactive aggregates and the availability of non-reactive aggregates is considered an issue. According to ACI (1998), avoiding reactive aggregates is not an economical option in many regions. It is thus important to: (1) know the service record of an aggregate source to determine if there is a potential problem and (2) conduct a condition assessment of concrete structures, with more than 10 years of service, that has a similar material composition and mixture proportions. Also, Thomas et al. (2017) enumerate different reasons why the use of non-reactive aggregates is not always possible:

- Non-reactive aggregates are not available locally;
- The cost of shipping non-reactive aggregates;
- Reactive aggregates that are otherwise wholly suitable for concrete are readily and abundantly available at lower cost and with more reduced environmental impact;
- Lack of confidence in the results of the laboratory testing as test results are ambiguous;
- Locally-available materials fail the very aggressive accelerated mortar bar test (ASTM C1260 2014), regardless of the true reactivity.

Thomas et al. (2013b, 2017) state that a combination of testing is required to ensure that aggregate sources are non-reactive. These testing normally starts with a petrographic examination [ASTM C295 (2012) or RILEM AAR-1.1 (2016) and AAR-1.2 (Fernandes et al., 2016)], then expansion testing on mortar bars [ASTM C1260 (2014) or RILEM AAR-2 (2016)] and on concrete prisms [ASTM C 1293 (2020) or RILEM AAR-3 (2016)], and ends with field performance. The authors also advise that these tests should be done regularly to know if the composition and therefore reactivity does not change in a pit or a quarry. But field performance survey is in practice rarely done. It is generally an alternative to laboratory testing but the requirements to obtain reliable results regarding the potential reactivity of aggregates from field performance surveys are quite stringent.

The quality of aggregates can be improved by a variety of means known as beneficiation (Rogers, 1989; Alexander and Mindess, 2005; Farny and Kerkhoff, 2007). Rogers (1989) commented that beneficiation methods are used in the case of some Canadian reactive aggregates. ACI (1998), based on different authors, enumerated several beneficiation strategies that could be employed for potentially-reactive aggregates. Farny and Kerkhoff (2007) also mention beneficiation strategies that may be able to remove a large portion of the reactive aggregates; however, such practices may also contribute to removing some of the good aggregates. Table 2.9 summarizes the different beneficiations processes.

RILEM AAR-7.1 (2016) recommends a precautionary measure (M2) to cover the blending of reactive and non-reactive constituents and thus ensure the use of non-reactive aggregate combinations. The RILEM Recommended methods should then be followed, in accordance with AAR-0 (2016), to identify such “non-reactive” aggregate combinations.

In RILEM AAR-0 (2016), for petrographical examinations, aggregate combinations are classified into three categories: (1) Class I—very unlikely to be alkali-reactive; (2) Class II—potentially alkali-reactive or alkali-reactivity uncertain; (3) Class III—very likely to be alkali-reactive. Some countries like Belgium, France, Germany and Portugal (Fernandes et al., 2017), and Denmark (Lindgård et al., 2017) have a threshold value of 2% for the quantity of reactive silica contained in concrete aggregates. For some countries, the presence of reactive species above 2% is not allowed (Figueira et al., 2019), while for others further testing (mortar bar test – ASTM C 1260 - 2014 or RILEM AAR-2 - 2016) must be done to assess the reactivity, and in Portugal also concrete prism tests are recommended (LNEC E 461, 2007). Figueira et al. (2019) mention that other countries do not have a limit for the quantity of reactive silica in the aggregate, and refer that additional tests should be done in the presence of reactive aggregates.

Table 2.9. Aggregate beneficiation (ACI 1998; Alexander and Mindess, 2005; Farny and Kerkhoff, 2007).

Aggregate beneficiation	Methodology	Example
Heavy media separation	Process that separates lighter materials from normal dense particles.	Separates coal and lignite from the rest Used in reactive material with low density, such as weathered opaline cherts
Rising-current classification	Process with the same purpose as heavy media separation, but involves separating more lighter materials	Separates wood and lignite from the rest. May remove a large portion of the reactive aggregate
Hydraulic jigging	Process more suited to separate particles with only small differences in relative density	May remove a large portion of the reactive aggregate
Crushing	Crushing of rock gives properly sized material	Removes soft and friable particles
Washing and scrubbing	Removes surface coating and finely divided material	Removes some reactive coatings Washing is effective in removing sodium or potassium salts from sea-dredged aggregates
Selective quarrying	Examines the source of aggregate <i>in situ</i> ensuring that only favourable material is finally processed	It is employed to avoid strata of rock that are identified as potentially reactive
Diluting aggregates	Blending reactive and non-reactive constituents	Limestone sweetening: replacing up to 30% of a reactive sand-gravel aggregate with crushed limestone, is effective in preventing deterioration in some sand-gravel aggregate concretes
Chemical treatment of aggregate (Hudec and Larbi, 1989)	Coating technique or chemical treatment	May reduce the potential reactivity of aggregate by neutralizing the reactive surface

Precautionary measure M2 alerts to the proportion of silica and the damage it can create, emphasizing the pessimum effect of different aggregates. In the same measure, importance is given to the assess the proposed aggregate combination, as amounts of reactive silica that are innocuous in either the fine or the coarse aggregate alone may be damaging in the combined aggregate. On the contrary, it seems that reactive fine or coarse aggregates may be safe when used in combination, which can be assessed by the RILEM methods AAR-3 (2016) and AAR-4.1 (2016). This precautionary measure ends by saying that when it is used correctly, the control of the “pessimum” effect can be an effective way of fighting ASR and allowing the use of available natural resources.

2.5.3. Minimize the alkali content of the pore solution

One of the procedures to prevent ASR is to minimize the concrete alkali content. This procedure permits to reduce of the hydroxyl ion concentration and consequently the pH of the concrete pore solution (ACI 1998). Fournier et al. (2016) indicate that the efficacy of low-alkali cement in controlling expansion due to ASR depends on the aggregate and is not necessarily a long-term solution against ASR.

There are several ways to reduce the alkali content of the concrete pore solution according to the precautionary measure M1 described in RILEM AAR-7.1 (2016):

- Limiting the alkali content of the concrete;
- Use of a low alkali cement;
- Include a sufficient proportion of low lime-fly ash, another pozzolana that demonstrated to be effective, or ground granulated blast furnace slag in the concrete.

The RILEM AAR-7.1 (2016) recommends that when there is potential for ASR to occur, an accepted allowable limit for the alkali content of the concrete should be used based on aggregate reactivity. This allows for national specifications to use an appropriate safety margin adapted to local experience. Table 2.10 show examples of using the aggregate reactivity categories to set alkali limits.

Table 2.10. Alkali limits for different aggregate reactivity categories (AAR-7.1, 2016).

Aggregate reactivity	Alkali limit (kg/m ³ Na ₂ O _{eq})
Low	None required
Medium	Typically 3.0 to 3.5 kg/m ³
High	Typically 2.5 to 3.0 kg/m ³

2.5.4. Supplementary cementitious materials (SCMs)

The SCMs also referred to as mineral additions, are widely used with Portland cement as blended cement or added separately at the ready-mixed concrete plants (Lothenbach et al., 2011; Ideker et al., 2019). The benefits of using SCMs are that they can:

- (1) reduce the CO₂ signature per m³ of concrete (Duchesne, 2006; Lothenbach et al., 2011; McCarthy and Dyer, 2019), which represents almost a ton of CO₂ emitted for every ton of cement produced (Duchesne, 2006; Lothenbach et al., 2011);

- (2) save non-renewable sources (Duchesne, 2006) ;
- (3) minimize waste (Duchesne, 2006; Lothenbach et al., 2011) and
- (4) improve the properties of concrete (Duchesne, 2006).

According to Fernandes and Broekmans (2013), the SCMs can act as an inert filler in the hydrated paste or form additional CSH by reacting with the excess portlandite; normally the beneficial effect of SCMs is coming from both the above actions, thus producing a denser, less permeable and stronger binder.

These materials are usually considered one of the most efficient means of controlling ASR (Thomas et al., 2013b). According to Thomas (2011), any SCMs can be used to control ASR as long as they are used in sufficient amounts generally as a cement substitute. However, the effectiveness of SCMs is dependent on different factors (Duchesne, 2006; Thomas, 2011; Thomas et al., 2013b):

- Mineralogical and chemical composition (more SCMs are required when silica content decreases or when alkali and calcium contents increase);
- The percentage used as cement replacement depends on the nature of the reactive aggregate to control, the more reactive the aggregate is, the higher the quantity of SCMs necessary);
- The concrete alkali content; the amount of SCMs required increases with an increase in the concrete alkali content;
- Exposure conditions of concrete during service; concrete exposed to external sources of alkalis, such as seawater or deicing chemicals, may require higher levels of SCMs.

SCMs include a range of natural and industrially manufactured materials with frequently pozzolanic behaviour (Ingham, 2011). Some of these materials correspond to industrial by-products that include fly ash (FA), silica fume (SF) or microsilica, rice husk ash (RHA) and ground granulated blast furnace slag (BFS) (Duchesne, 2006; Thomas et al., 2013b). BFS is not considered a pozzolanic material (McCarthy and Dyer, 2019) but rather correspond to a hydraulic or cementitious material. Metakaolin (MK) and calcined clays (CC) are pozzolanic materials of growing interest worldwide; they are produced by temperature treatments of natural clays, slates, shales, etc. The use of pozzolans dates back to Roman times when it was discovered and a variety of pozzolans was used in lime mortars in different structures throughout the coastlines of the Mediterranean Sea (ACI, 1998).

According to Glasser (2012), the use of SCMs in concrete has been one of the major success stories in concrete technology over the past 40 years. The author however emphasizes that the future progress of SCMs depends on: (1) the continued availability at a low cost of SCMs, (2) their classification as non-toxic waste and (3) increasing their use in concrete applications.

Thomas (2011) and Thomas et al. (2017) indicate that the level of SCMs required for preventing ASR usually increases with the following factors:

- an increase in the alkalis available from the Portland cement; if significant alkalis are available from the aggregates (e.g., feldspars, greywackes) or external sources, this will likely also increase the level of SCMs required;
- an increase in the alkali content of the SCMs;
- an increase in the CaO-to-SiO₂ ratio of the SCM;
- an increase in the reactivity level of the aggregate.

However, Rajabipour et al. (2015) state that the use of SCMs presents some challenges:

- The high replacement levels of portland cement with SCMs can influence negatively some concrete properties that include setting, strength development and freeze-thaw/scaling durability, especially in cold construction season;
- the availability of high-quality SCMs in some locations has become uncertain due to the use of natural gas or other fuels rather than coal in the power plants, and also because of new environmental regulations that result in the production of ashes that do not meet any more concrete specifications.

Among the SCMs, silica fume and metakaolin are the ones that have the highest amounts of reactive silica and that only require low levels of replacement (e.g., 10 -15%); on the contrary, Class C fly ash and GGBS contain lower quantities of silica and need higher levels of replacement (e.g., $\geq 40\%$) (Thomas et al., 2017). Thomas (2011) affirms that SCMs with low CaO and low alkali contents have shown to be the most effective in preventing ASR.

The beneficial effect of SCMs in preventing ASR mainly comes from the fact that they consume a portion of the alkalis and calcium from Portland cement, thus reducing the pH of the pore solution and the availability of such elements for reacting with the aggregate (Thomas et al., 2013b, 2017). SCMs also contribute to reducing the permeability of hydrated cementitious systems, which is also beneficial in slowing down or preventing ASR.

Blast furnace slag (BFS)

Blast furnace slag (BFS) is a non-metallic by-product made during the production of iron by a thermochemical reduction in a blast furnace (Moranville-Regourd and Kamali-Bernard, 2019) used in steel making (Kosmatka and Wilson, 2011). Blast furnace operates at a temperature of around 1500° C to melt iron oxide, coke, and fluxing stone (limestone or dolomite), thus producing molten iron and molten slag (Panesar, 2019). Different by-products can be obtained from the various processes used in cooling the molten slag (Moranville-Regourd and Kamali-Bernard, 2019):

- Air-cooled blast furnace slag (ABS). The BFS when cooled slowly in the air solidifies into a grey crystalline stony material known as “air-cooled” or crystalline blast furnace slag. It is commonly used as a road foundation aggregate material and as a concrete aggregate;
- Blast furnace slag pellets. The BFS when cooled quickly in the air can result in the following products: (1) layered pellets (>10mm) that occur as nodules with a porous structure; they are partly crystalline and are used as lightweight aggregate; (2) a smaller fraction (<10mm), mostly glassy in nature, and that can be ground to be used as a hydraulic constituent of blended cement.
- Granulated blast furnace slag (GBS). The BFS when cooled very rapidly solidifies as a glassy granulated mass into a granulator. The GBS is poured into a large excess of water (100m³/t of slag) or subjected to water jets under 0.6MPa pressure (3m³/t of slag). The water content of slag (≤30%) is then largely eliminated in dryer mills or filter basins to produce vitrified granules (0–5mm). The above granules are then ground separately to produce ground granulated blast furnace slag (GGBS) or together with Portland cement clinker to produce a blended cement for use in mortars and concretes.

In terms of slag activation, ordinary air-cooled slag has no (Kosmatka and Wilson, 2011), or very little cementitious properties (Moranville-Regourd and Kamali-Bernard, 2019); on the other hand, ground granulated blast-furnace slag (GGBFS) has latent hydraulic properties that could be activated using suitable activators (Allahverdi et al., 2011) like lime, Portland cement, alkalis such as caustic soda or sodium carbonate, sodium phosphate or the sulfates of alkalis, calcium or magnesium (Moranville-Regourd and Kamali-Bernard, 2019).

BFS is mainly composed of silicates and aluminosilicates of calcium; however, the chemical composition of BFS is dependent on different parameters, including (Moranville-Regourd and Kamali-Bernard, 2019): (1) the nature of the ore, (2) the composition of the limestone flux, (3) the coke consumption and (4) the kind of iron being made. The above authors also mention that the chemical composition of BFS can vary over the years due to variations in the sources

and types of ore smelted, which will affect the major (lime, silica, alumina and magnesia) and minor components (sulfur in the form of sulfides, and ferrous and manganese oxides). Table 2.11. shows the range of values for the chemical composition of GGBFS from three different countries based on the work of Özbay et al. (2016).

Several properties of concrete can be improved through the use of BFS, including (Figueira et al., 2019): abrasion resistance, workability, long-term compressive strength, shrinkage, permeability and water diffusion, chloride ions and gas diffusion reduction, resistance to sulphate attack and ASR prevention. The reported advantages of using BFS given ASR prevention include: reduction in permeability (Panesar, 2019), dissolution and consumption of the alkalis (Panesar, 2019) or alkali retention (Figueira et al., 2019) or reduction of alkalinity in the pore solution (Özbay et al., 2016), Ca(OH)_2 consumption (Özbay et al., 2016; Panesar, 2019). However, the efficiency of BFS in preventing ASR depends on the nature of GGBFS, the aggregate reactivity level and the Portland cement alkali content (Özbay et al., 2016).

Table 2.11. Chemical composition of GGBFS from three countries (Özbay et al., 2016).

Chemical element (%)	USA	South Africa	Turkey
CaO	29–50	30–40	34–41
SiO₂	30–40	30–36	34–36
Al₂O₃	7–18	9–16	13–19
Fe₂O₃	0.1–1.5	–	0.3–2.5
MgO	0–19	8–21	3.5–7
MnO	0.2–1.5	–	1–2.5
S	0–2	1–1.6	1.2
SO₃	–	0	–

Several field and laboratory studies have shown the efficiency of replacing 50% or more of the Portland cement with BFS for preventing ASR (Lindgård et al 2012). Grattan-Bellew and Katayama (2017) reported that a cement replacement of 40% by BFS did not suppress cracking due to late expansive ASR in a mass concrete structure in Japan. Katayama (2008) also reported that replacing 50% of Portland cement with Japanese BFS reduced expansion by 30% though it did not prevent the formation of cracks with ASR gel at later ages. Hooton et al (2000) reported limited (i.e. < 0.10%) accelerated mortar bar expansion at 49 days for a 50% slag mixture incorporating a marginally reactive aggregate (Figure 2.12).

Lindgård et al. (2012) indicate that the role of slag in reducing ASR expansion is not yet fully clarified, despite the number of studies conducted regarding the mechanism of GGBFS towards ASR.

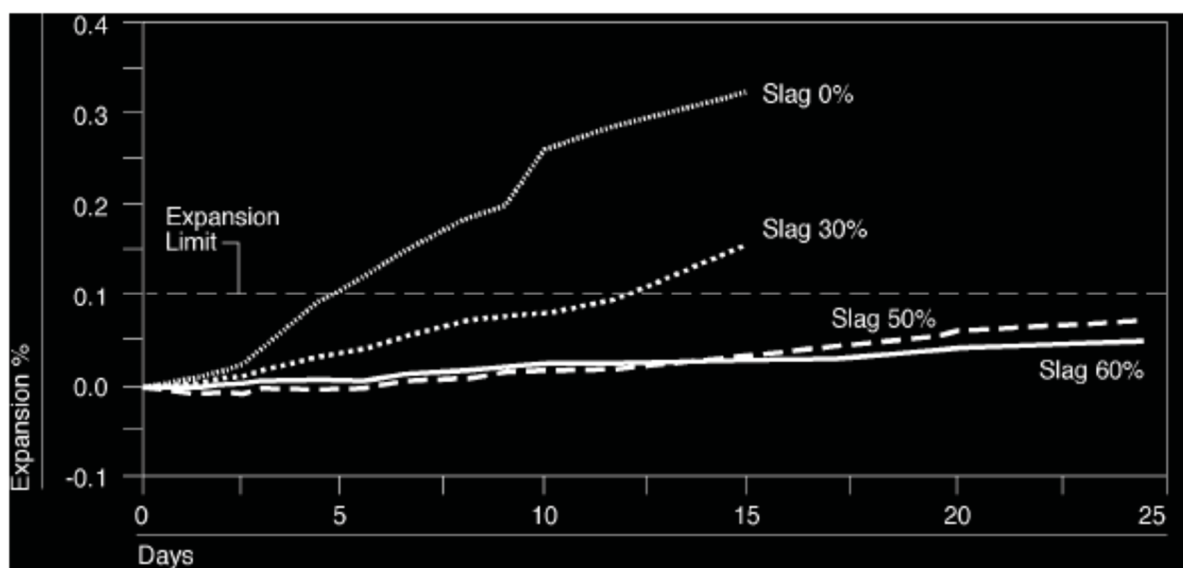


Figure 2.12. Expansion evolution of accelerated mortar bar tests performed on samples prepared with various slag replacement levels (Hooton et al., 2000).

Fly ash (FA)

Fly ash is produced by burning pulverized coal, and lately in combination with other organic materials or co-fuels, in electric power generating plants (McCarthy and Dyer, 2019). At approximately 1600° C, coal's mineral impurities (e.g., clay, feldspar, quartz, and shale) fuse in suspension within the exhaust gases, and they are expelled from the combustion chamber; through cooling, the fly ash solidifies into glassy particles that are collected in electrostatic precipitators as a finely divided powder (Kosmatka and Wilson, 2011).

Fly ash characteristics depend on the type of coal (anthracite, bituminous, subbituminous and lignite) used in the burning conditions and the collection system (McCarthy and Dyer, 2019). Panesar (2019) further indicates that variations in fly ash characteristics are influenced by the mineralogical composition of the coal, degree of coal pulverization, type of furnace, combustion temperature, oxidation conditions, and the collection, handling, and storage conditions; The chemical and physical characteristics and mineralogical composition of fly ash can vary from plant to plant, and even with changing in the conditions described above within the same plant.

From the point of view of chemical composition, FA is composed mainly of SiO_2 and CaO (Holland et al., 2016), although the quantity of CaO is very variable based on the origin of the coal (Lothenbach et al., 2011); it also contains significant amounts of Al_2O_3 . Kosmatka and Wilson (2011) report that fly ash is mostly composed of alumino-silicate glass containing silica, alumina, iron, and calcium, with minor amounts of magnesium, sulfur, sodium, potassium, and carbon. Panesar (2019) mentions that the carbon content in FA, measured by the loss-on-ignition (LOI), corresponds to the incomplete combustion of the coal and/or the presence of organic additives.

In accordance with ASTM C 618-15 (2019), McCarthy and Dyer (2019) describe different classes of FA based on the type of coal used and on the presence of major oxides: (1) Class F fly ash, is siliceous and is obtained by burning bituminous coals, with the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$ and low calcium oxide content; (2) Class C fly ash is calcareous and normally derived from subbituminous coals or lignite, with the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 50\%$ and high calcium oxide content. The correspondence between coal type and fly ash classes is however not always applicable/relevant. CSA A3001 (CSA, 2013) defines three categories of fly ashes based on the CaO content: Low-calcium fly ash (Type F) – $\text{CaO} < 15\%$, moderate-calcium fly ash (Type CI) – $15\% \leq \text{CaO} \leq 20\%$, and high-calcium fly ash (Type CH) – $\text{CaO} > 20\%$.

When combined with the Portland cement and water, fly ash reacts primarily through a pozzolanic reaction with Ca(OH)_2 , thus resulting in a denser binder microstructure with time (Holland et al., 2016). The glass with low-calcium fly ash (Class F) is an aluminosilicate that will not react with water except if there is some activator present like the calcium hydroxide (Ca(OH)_2) (Kosmatka and Wilson, 2011). In the case of class C fly ash, the calcium is combined with the glass which makes it react directly with the water, thus becoming a hydraulic SCM.

Class F fly ashes are more abundant than the other types (Lothenbach et al., 2011); they are widely considered to improve the resistance of concrete against sulphate attack and ASR (Holland et al., 2016). Thomas et al. (2011) reported that concrete resistance is generally improved by the addition of low calcium or Class F fly ash, especially in the long term.

Shehata and Thomas (2000) studied the effect of fly ash on the expansion due to ASR. The authors tested mainly concrete prisms (CSA A23.2 Test 14A, 2014) containing a reactive aggregate and different types and levels of fly ash. The aggregates included a reactive siliceous limestone (Spratt) used as coarse aggregate and nonreactive natural sand. Figure

2.13 shows the 2-year expansion test values of concrete specimens made with various fly ashes at different replacement levels.

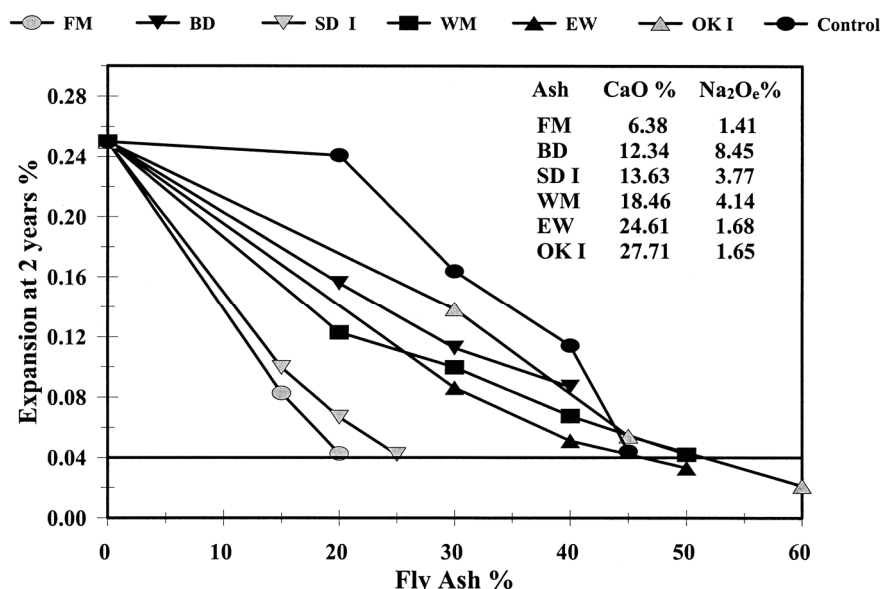


Figure 2.13. Effect of ash composition (Type F fly ash: FM; Type CI fly ash: BD, SD I, WM; Type CH fly ash: EW, OK) and of replacement level on expansion due to ASR. (Shehata and Thomas 2000).

The authors concluded that the partial replacement by fly ash did not lead to an increase in expansion despite of the different compositions of the fly ash selected. In all cases, the expansion of the fly ash concretes is less than that of the control concrete at the same alkali content. The data showed that the proportion of fly ash required to reduce concrete prism expansion below the expansion limit of 0.040% at two years increases with an increase in the CaO content and the alkali content of the FA.

Thomas (2011) showed that low-calcium and low alkali fly ashes are more efficient in binding alkalis in pozzolanic hydrates, thus resulting in larger reductions in the pH of the pore solution.

Metakaolin

Metakaolin is a pozzolan produced by the thermal treatment (e.g., calcination) of the clay mineral kaolin or kaolinite at temperatures in the range of 650/700-800°C (Ramlochan et al., 2000; Kosmatka and Wilson, 2011; McCarthy and Dyer, 2019). It is commonly used as cement replacement in concrete, but is also used in the production of ceramics (Holland et al., 2016).

One of the singularities of metakaolin is that it is not an industrial by-product but rather a natural material that was subjected to thermal treatment (Menshaz et al., 2017).

Metakaolin is an aluminosilicate material where the major chemical constituents are silicon dioxide (SiO_2) and alumina oxide (Al_2O_3); other components such as ferric oxide, calcium oxide, magnesium oxide, and potassium oxide are also part of the composition of metakaolin (Juenger et al., 2012); however, the composition of metakaolin can vary according to different sources of kaolin. According to Kakali et al. (2001), metakaolin has a highly disordered structure, which gives it excellent properties as SCM. The pozzolanic character of metakaolin is highly associated with the crystallinity of the original kaolinite. Exposing kaolin to long calcination times (5 or 15 h above 650°C) decreases its pozzolanic activity after 7 days (Bich et al., 2009). Metakaolin is one of many SCMs that contribute to reducing the expansion of concrete by incorporating potentially reactive aggregates down to the safe level (Falikman and Rozentahl, 2017). Ramlochan et al. (2000) showed that the incorporation of only 20% reduced significantly the concentrations of OH^- , Na^+ and K^+ in the pore solution of paste specimens. The authors showed that the expansion of mortar bars (CAN/CSA A23.2-25A) containing 15% and 20% metakaolin did not cross the expansion limit of 0.10% at the end of 14 days for both the highly-reactive Spratt aggregate (Figure 2.14A) and the moderately-reactive Sudbury aggregate (Figure 2.14B).

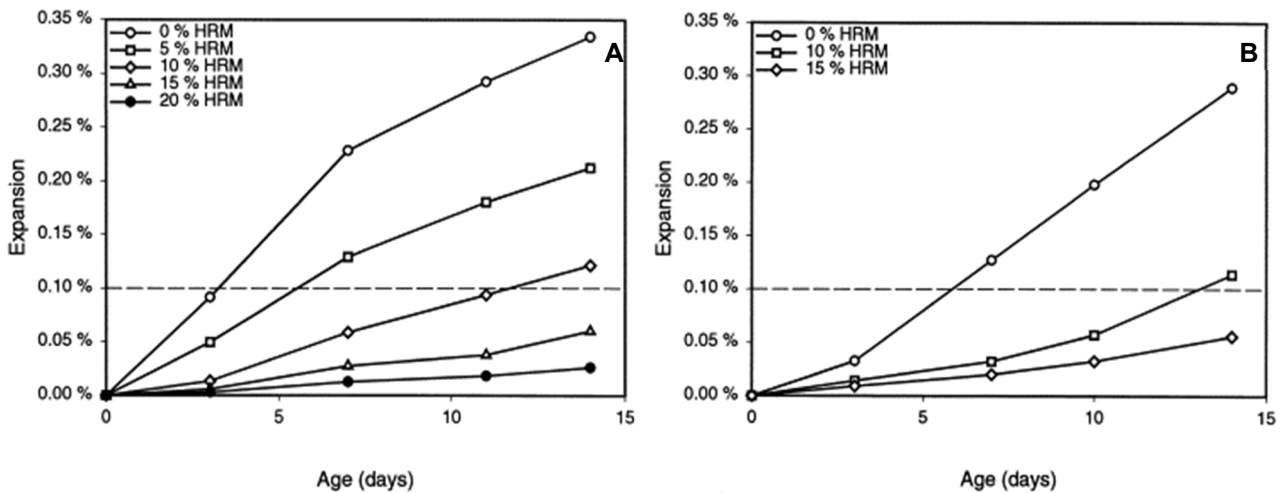


Figure 2.14. Expansion evolution of mortar bars containing different levels of highly reactive metakaolin (HRM) as cement replacement: a) with Spratt aggregate and b) Sudbury aggregate (Ramlan et al 2000).

In the same work, concrete prisms were prepared according to the Canadian standard CSA A23.2-14A (concrete prism method) and stored at 38°C and 100% RH. Once again, the reactive aggregates used in the mixes included the moderately-reactive Sudbury gravel (Figure 2.15A) and the highly-reactive Spratt siliceous limestone (Figure 2.15B). The results showed that the two-year expansion of the test prisms containing 10% and 15% HRM with the Sudbury aggregate, and 15% and 20% HRM with the Spratt aggregate did not cross the 0.040% expansion limit.

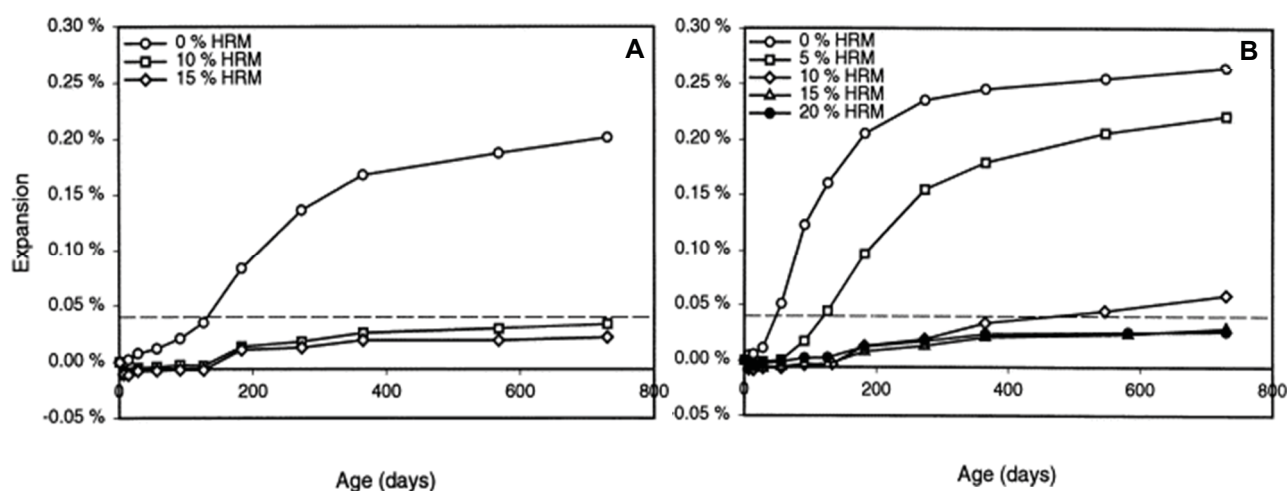


Figure 2.15. Expansion evolution of concrete prisms containing different levels of highly reactive metakaolin (HRM) as cement replacement: A) Sudbury aggregate, B) Spratt aggregate (Ramlochan et al., 2000).

Silica fume

Silica fume (SF), also known as microsilica or condensed silica fume (Lewis and Fidjestøl, 2019), is a by-product of the manufacture of silicon metals and ferrosilicon alloys (Kosmatka and Wilson, 2011) in electric-arc furnaces at temperatures up to 2000°C (McCarthy and Dyer, 2019).

SF is mainly composed of silicon dioxide although it can contain a significant quantity of iron (if the origin is a ferrosilicon furnace) and small amounts of some other elements (1% and less) (Lewis and Fidjestøl, 2019). McCarthy and Dyer (2019) indicate that the silicon metal process gives purer products (high SiO₂ content), while the production of ferrosilicon alloys has more complex compositions and the content in other elements can reach as high as 30%. Table 2.12 shows the range in the chemical composition of SF from the production of Silicon Metal and 75% ferrosilicon alloy based on the work of Hjorth (1982).

Some of the main characteristics of SF are (Boddy et al., 2000):

- small particle size of 0.1 μm (about 100 times smaller than the Portland cement particles);
- high specific surface area (20 000 m^2/kg while Portland cement has values typically ranging from 300 to 500 m^2/kg);
- a high amorphous silica composition.

Table 2.12. Chemical composition of silica fume from the production of silicon metal and 75% ferrosilicon alloy (Hjorth, 1982).

	Si Metal	75% FeSi
SiO₂, %	94–98	86–90
C, %	0.2–1.3	0.8–2.3
Fe₂O₃, %	0.02–0.15	0.3–1.0
Al₂O₃, %	0.1–0.4	0.2–0.6
CaO, %	0.08–0.3	0.2–0.6
MgO, %	0.3–0.9	1.0–3.5
Na₂O, %	0.1–0.4	0.8–1.8
K₂O, %	0.2–0.7	1.5–3.5
S, %	0.1–0.3	0.2–0.4
LOI, %	0.8–1.5	2.0–4.0

SF is a strongly pozzolanic material, both in terms of its capacity for binding lime and its reaction rate.

According to Lindgård et al (2012), SF is among the most efficient SCMs for reducing ASR expansions even when used at low replacement levels (8–10%); however, the authors highlight that the quantity used to avoid ASR is dependent on the reactivity level of the aggregate. Lewis and Fidjestøl (2019) state that SF binds the alkalis from the pore solution and contributes to the reduction of concrete permeability, being less water available. These two factors working together help to prevent ASR expansion.

Several references report that the use of SF helped solve a severe ASR problem in Iceland several decades ago (Ásgeirsson, 1986; Ólafsson, 1989; Guðmundsson and Ólafsson, 1996; Guðmundsson and Ólafsson, 1999; Guðmundsson and Ólafsson, 2002). Ásgeirsson (1986) tested different mortar bars containing reactive Hvalfjörður sand and different replacement levels of the ordinary Portland cement (OPC) by SF (5%, 7.5%, 10%) and by a natural pozzolan (metamorphic rhyolitic rock; 10%, 15% and 25%). The results showed that the use of 15% and 25% of natural pozzolan (R) and 7.5% and 10% of SF was effective in keeping the expansion

of the mortar bars below 0.10% at the end of four years of testing (Figure 2.16), which were the values judged adequate to control ASR.

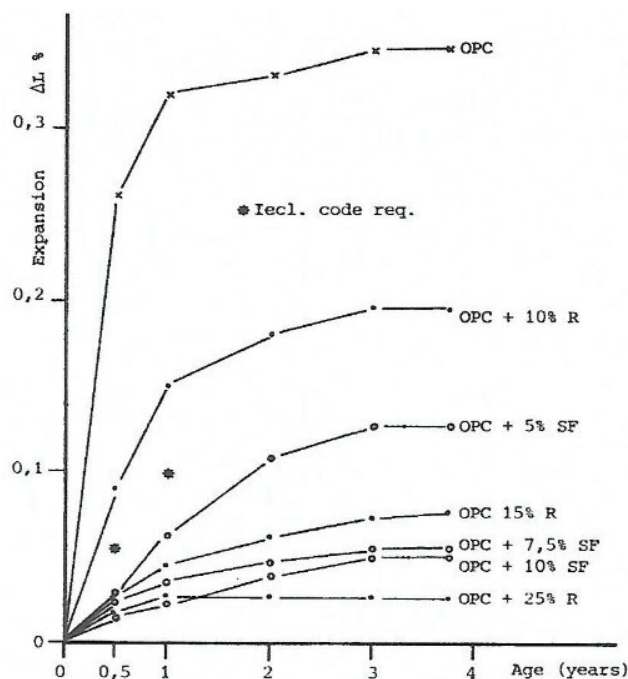


Figure 2.16. Expansion evolution of mortar bars containing Ordinary Portland Cement with microsilica (MS) and natural pozzolan (R) both at different replacement values (Ásgeirsson, 1986).

Another study conducted by Boddy et al. (2000) involved the testing of concrete prisms according to Canadian standards CSA A23.2-14A, with a reactive siliceous limestone aggregate (Spratt) and different types and replacements of SF (4, 8 and 12%). The results obtained (Figure 2.17) showed that 4% SF did not prevent long-term expansion due to ASR with all SF investigated.

The use of 8% SF considerably reduced expansion compared to the control but was insufficient to bring expansions below 0.040% after 1 year of testing. The use of 12% SF was effective in reducing expansion below 0.040% expansion after 1 year.

Table 2.13 summarizes the chemical composition, benefits and level required for preventing ASR for each type of SCMs.

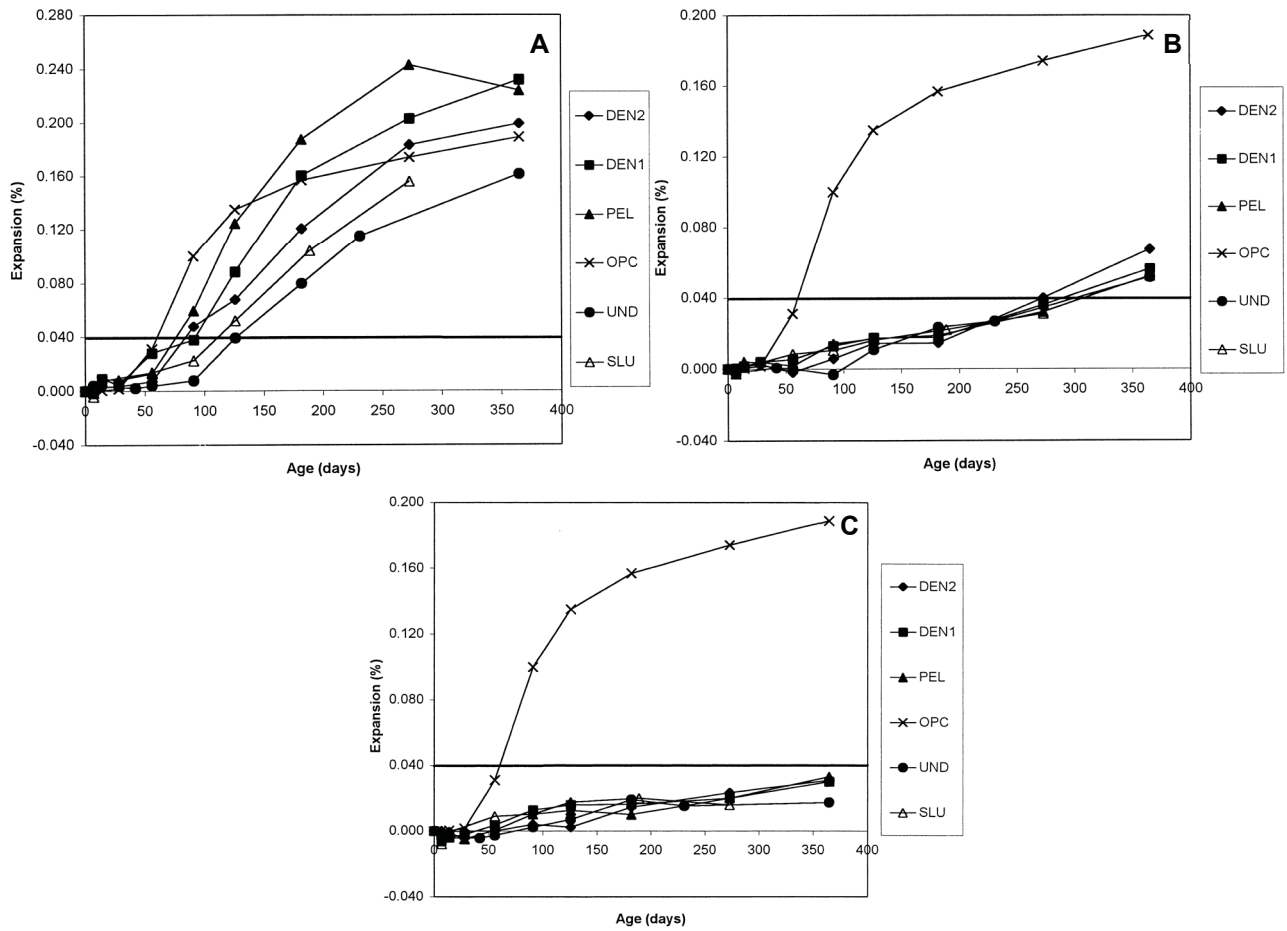


Figure 2.17. Expansion of concrete prisms containing: A) 4, B) 8 and C) 12% SF as replacement of the OPC (Ordinary Portland cement). The different types of SF used are as follows: SF from Canada: UND – Undensified, PEL-Pelletized, DEN1 - Densified #1; SF from the USA: DEN2 - Densified #2, SLU – Slurried) (Boddy et al., 2000).

Table 2.13. Chemical composition, benefits and level required to prevent ASR for each type of SCMs.

Type of SCM	BFS	FA		SF	MK
Chemical Composition (Panesar, 2019)		Low-calcium	High-calcium		
CaO (%):	29.0-43.7	0.5-19.3	21.2-62.9	0-0.8	0-3.4
SiO ₂ (%):	30.0-40.0	37.0-62.1	11.8-46.4	> 85	50.6-74.3
Al ₂ O ₃ (%):	6.0-19.3	15.3-35.6	2.6-20.5	0-1.1	17.8-46.9
Fe ₂ O ₃ (%):	0.1-2.5	2.6-24.8	1.4-15.6	0-2.0	0.5-1.2
MgO (%):	0-19.0	0-5.4	0.1-6.1	0-4.5	0.1-0.3
K ₂ O (%):	0.3-0.5	0.1-7.8	0.3-9.3	0-1.3	0.2-1.1
Na ₂ O (%):	0-1.2	0.1-7.9	0.2-2.8	0-1.3	0.1-0.3
SO ₃ (%):	1-4.0	0-4.9	0.9-12.9	0-1.3	0-0.03
LOI (%):	0.1-1.7	0.2-32.8	0.1-11.7	0-2.8	1-2.6
Benefits regarding ASR (Panesar, 2019)	- Reduces permeability; - consumption of the alkalis, - reduction in the amount of calcium hydroxide	- alkali binding, - reduces calcium hydroxide in the system, - reduces the aggregate dissolution - reduces permeability	- rapidly combines with alkalis present in the pore solution	- entraps alkalis, - decreases the pH of the pore solution	
			- incorporates the alkalis as substitutes for calcium in the calcium silicate hydrate matrix, - reduces the permeability of concrete by impeding the entry of water and therefore less water available.	<i>Figueira et al. (2019):</i> - seems to be effective in reducing Ca(OH) ₂ and reduces ionic mobility - can absorb alkalis	
Level required (%) (Thomas et al., 2017)	35-65%	Low-calcium fly ash (< 15% CaO): 20 – 30%		8-15%	10-20%
		Moderate-calcium fly ash (15 - 20% CaO)*: 25 - 35%			
		High-calcium fly ash (> 20% CaO)*: 40-60%			

BFS: Blast furnace slag; FA: Fly ash; SF: Silica fume or microsilica; MK: Metakaolin; * Higher levels may be required if Na₂O_{eq} levels > 4.5%.

2.5.5. Lithium-based compounds

Lithium belongs to the alkali metal group together with sodium and potassium. Lithium does not occur naturally in the environment being commonly found in lithium-bearing minerals (e.g., spodumene, petalite, lepidolite), in pegmatite rocks, or as dissolved salts like lithium chloride (LiCl) (Thomas et al., 2007).

The use of lithium for preventing ASR dates back to the 1950s when it was studied by McCoy and Caldwell (1951). These two authors tested more than 100 different compounds and found that various salts of lithium (e.g., LiCl, Li_2CO_3 , LiF, Li_2SiO_3 , LiNO_3 , and Li_2SO_4), were the most effective in reducing the expansion of mortar bars (ASTM C 227) incorporating a highly reactive Pyrex glass (Thomas et al., 2013b; Rajabipour et al., 2015; Thomas et al., 2017). Since then, very few studies were conducted regarding lithium until the end of the 1980s (Rajabipour et al., 2015). As listed in the review of Figueira et al. (2019), some studies worth of mention include the following: Sakaguchi et al. (1989) and Ohama et al. (1989), both in the proceedings of the 8th ICAAR; Stark (1993) in the scope of the SHRP program in the USA; Diamond (1999), available in Cement and Concrete Research Journal; Lane (2002) in a report from the Virginia Transportation Research Council; Kawamura and Fuwa (2003), Mo et al. (2003), Collins et al. (2004) and Bérubé et al. (2004), all in Cement and Concrete Research Journal; Feng et al. (2006) and Tremblay et al. (2006), both presented in the Marc-André Bérubé symposium on AAR in concrete.

The use of lithium-based products proved to be effective in reducing ASR expansion when used at $[\text{Li}]/[\text{Na}+\text{K}]$ molar ratios ≥ 0.74 (Thomas et al., 2007), which is considered the standard dose by lithium-based products manufacturers (Thomas et al., 2007, 2017) to efficiently suppress ASR expansion (Feng et al., 2005). However, Tremblay et al. (2006) showed that this dosage might not be efficient for all aggregate types. Feng et al. (2006) showed that lithium was not effective for concrete containing greywacke aggregate even when the lithium-to-alkali ratio was doubled (i.e. $[\text{Li}]/[\text{Na}+\text{K}] = 1.48$). Feng et al. (2005) showed that lithium salts are more effective with highly-reactive aggregates than with slowly-reactive aggregates.

Among all the lithium salts tested, it seems that the one with better results in suppressing ASR is lithium nitrate (LiNO_3) (Thomas et al., 2013b, 2017), which is one of the most studied compounds tested in different content (Figueira et al., 2019). According to Feng et al. (2005), this lithium salt does not introduce more OH^- ions in the pore solution (compared to lithium hydroxide monohydrate); it is soluble and has a neutral pH, which makes it safe to handle.

Tremblay et al. (2006) attribute to LiNO_3 some other advantages like not being susceptible to pessimum effects and not increasing the pH of the pore solution.

Many theories have been proposed for explaining the beneficial effect of lithium against ASR. Feng et al. (2010) explained that when LiNO_3 is used, a layer with Li-Si crystals is formed at the surface of the reactive SiO_2 particle and a gel is formed (Figure 2.18). This layer works as a diffusion barrier that protects the reactive aggregate particles from attack by the alkalis. The gel formed has different characteristics compared to conventional ASR gel; it is a Li-bearing low-Ca ASR gel and presents a denser structure, stronger bound with the aggregate particles and lower mobility. Thomas et al. (2013b, 2017) suggest that the lithium compounds change the nature of the reaction product. RILEM recommendation AAR-7.1 (2016) states that the lithium salts added to the mixing water work by modifying the nature of the ASR gel into a gel that does not absorb water and does not exert deleterious expansive force.

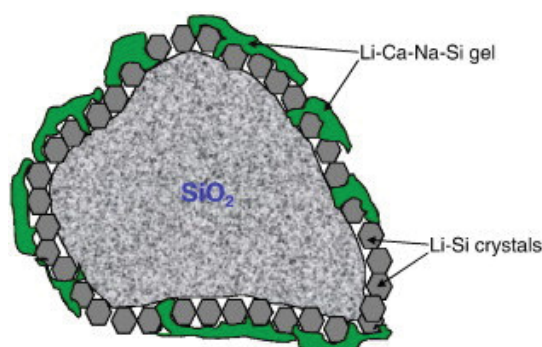


Figure 2.18. Schematic mechanism of ASR when Li is present (Feng et al., 2010).

Sakaguchi et al. (1989) studied the effects of lithium-based compounds on ASR by using mortar bars containing either pyrex glass or natural reactive aggregates (andesite); the authors concluded that lithium was effective in both cases. They also studied the inhibition effect of lithium by impregnating concrete prisms and mortar bars with symptoms of ASR with lithium (LiNO_2) solution; they found that any further expansion could be retarded or inhibited with the presence of lithium. They also confirmed that the lithium compound was involved in the chemical reaction and inhibited the formation of an alkali-silica gel.

Feng et al. (2005) concluded that the minimum $[\text{Li}]/[\text{Na}+\text{K}]$ to be used with efficacy to control ASR depends on the form of the lithium compound used, the nature of the reactive aggregate to control and probably the testing method used for evaluating that efficacy in the laboratory.

CHAPTER 3

ALKALI-SILICA REACTION IN VOLCANIC AGGREGATES

3.1. Case studies

Volcanic rocks such as andesites, rhyolites and basalts have been considered reactive in several countries either by their use as concrete aggregates in different structures affected with ASR or confirmed by different test methods conducted in the laboratory. ASR caused by volcanic aggregates has affected a significant number of concrete structures in countries such as Argentina, Iceland, Japan and Turkey, among others. In most cases, signs of ASR were associated with the use of andesites (Folliard et al., 2006; Tremblay et al., 2012; Yamada and Miyagawa, 2017) or rhyolites (Folliard et al., 2006; Tremblay et al., 2012; Fernandes et al., 2017) and not basalts. There are very few reports and papers in the literature on concrete structures affected by ASR due to the use of basalts, which include some cases in Argentina, Iceland and one case in Portugal. There are also some reports from Brazil where basalt was causing ASR (Fairbairn, 2017) but it is not very clear whether the problem was ASR.

In addition, several published works from several countries confirmed the potential alkali-reactivity of local volcanic aggregates. Argentina, Australia, Brazil, Czech Republic, Iceland, Japan and Turkey are among the countries where aggregates such as andesites, basalts and rhyolites were identified as potentially reactive or reactive through the use of petrographic examination and expansion tests (AMBT and CPT). Also, there are references (e.g. Robertson and Shen, 2018) to an outdoor exposure site in Hawaii where different concrete blocks of different mix designs are exposed to local weather conditions to evaluate the potential reactivity of local aggregates.

It is known that the reactivity of volcanic rocks depends on the presence (or not) of components considered deleterious. Wakizaka (2000) affirms that the reactivity of volcanic rocks is controlled by the presence of tridymite, cristobalite and volcanic glass and is affected by the formation age of the rocks. According to RILEM AAR-1.1 (2016), the reactivity of the andesite, rhyolite and basalt has been attributed to cristobalite and tridymite, interstitial glass in the matrix, or devitrified glass, opaline silica or chalcedony from low-temperature alteration. Katayama (2010) emphasizes that rhyolitic glass is considered reactive even if present in andesite, basalt or rhyolite, while basaltic volcanic glass is considered innocuous. Other authors state that clay minerals, especially montmorillonite, are considered deleterious (Maiza et al., 1995; Couto, 2008; Tiecher et al., 2018; Marfil et al., 2010; Rocco, 2012a; Rocco, 2012b; Marfil et al., 2013). Chlorophaeite is another component considered deleterious by different researchers (Hasparyk, 1999; Couto, 2008; Munhoz and Cincotto, 2008; Mizumoto, 2009).

3.1.1 Concrete structures made with volcanic aggregates

Several examples of concrete structures affected by ASR due to the use of volcanic aggregates are described in this section. These cases were reported from different countries such as Argentina, Brazil, Iceland, Japan, Portugal, Turkey and the United States of America, although the case in Brazil remains uncertain.

Argentina - Basalts

The first case of ASR reported in Argentina has been associated with the use of reactive sands from the Paraná River in a concrete pavement road (La Plata-Punta Lara) built in 1949-1950 (Milanesi et al., 2018).

Marfil and Maiza (2006) point out that some of the concrete deterioration detected in the Patagonia region is due to the local (severe) climatic conditions (extreme temperatures, wind and water action). Besides this, the authors refer to other factors that contribute to the concrete deterioration, such as inadequate curing of the concrete, sulphate attack and ASR.

The alkali-silica reactivity of basalts has been attributed to volcanic glass, either fresh or altered, clay minerals (e.g. montmorillonite) or silica minerals. Clay minerals have been the subject of several papers (Maiza et al., 1995; Marfil and Maiza, 1996; Maiza et al., 2005; Marfil et al., 2005; Maiza et al., 2006a), being recognized as an alteration product of volcanic glass (Milanesi, 2008; Madsen et al., 2019). Milanesi (2008) states that the devitrification of volcanic glass if its composition is acid enough, leads not only to the formation of smectite but also to the precipitation of cristobalite and tridymite. According to several researchers (Batic et al., 1994; Marfil et al., 2010), clay minerals contribute to the alkali-silica reactivity in concrete and are considered potentially reactive minerals. However, Milanesi (2008) affirms that clay minerals, especially those from the smectite group, have no direct relation with ASR and should not be considered as potentially reactive minerals. This is supported by RILEM AAR-1.1 (2016), which states that concrete damage from expanding clay minerals is not regarded as an alkali-silica reaction, even when alkalis may have contributed to the swelling.

In Argentina, there are some reported cases of ASR-affected concrete structures due to the use of basaltic aggregates. These cases are (1) a concrete dam (Marfil et al., 2005); (2) a section of the National Road 127 (Milanesi et al., 2008; Maiza et al., 2010); (3) pavements in Curuzú Cuatiá city (Maiza et al., 2010; Madsen et al., 2019) and (4) a runway concrete pavement in the airport of Corrientes city.

(1) Dam

The first case was studied in 1998 and corresponds to a concrete dam with an advanced state of deterioration. A petrographic study conducted on concrete cores concluded that the coarse aggregate was composed of basalts that were mainly suffering from an argilization process with abundant secondary montmorillonite and subordinate chlorite. This case was reported by Marfil et al. (2005), but there is no mention of the construction date, the location of the dam and no detailed information from the petrographic examination of the concrete.

(2) Concrete pavement of the National Road 127

The second case, studied by Milanese et al. (2008) and by Maiza et al. (2010), is related to a deteriorated pavement on National Road 127, located in the south of the province of Corrientes, between Entre Ríos and Cuatro Bocas, in the region of the Mesopotamia. This concrete pavement was constructed between 1996 and 1997; basalts were used as coarse aggregates and natural siliceous sand as fine aggregates (Milanese et al., 2008). The construction was made in different sections: (1) first it was used a low alkali cement ($< 0,6\% \text{Na}_2\text{O}_{\text{eq}}$) in the initial part of section I because the basalt was considered potentially reactive; however, at the same time laboratory tests were conducted, where the results obtained allowed to use a moderate alkali cement ($0,75\% \text{Na}_2\text{O}_{\text{eq}}$) in the rest of section I and sections II and III; (2) a high alkali cement ($> 1,0\% \text{Na}_2\text{O}_{\text{eq}}$) was used in section IV. After 10 years of service, only section IV presented signs of ASR and it was studied by Milanese et al. (2008) and by Maiza et al. (2010).

The visual inspection of some of the sectors of the concrete pavement revealed the presence of longitudinal cracks, map-cracking, discolouration and gel exudations (Maiza et al., 2010). Maiza et al. (2010) identified cryptocrystalline silica inside cracks and in the aggregate-cement paste interfacial zone. The petrographic examination of cores highlighted the presence of cracks filled with gel and crossing the coarse aggregates and the cement paste; also, air voids filled with deposits of gel and ettringite were observed (Milanese et al., 2008). Reaction rims were also found surrounding the basaltic aggregate particles. Maiza et al. (2010) also reported the presence of expanding clay minerals, chlorites, celadonite, zeolites and cryptocrystalline silica in the basaltic aggregates. In the fine aggregates, the siliceous sand presented reaction rims and microcracks.

(3) Concrete pavement of Curuzú Cuatiá

The third case is related to a pavement in Curuzú Cuatiá city constructed in 1997. This case was studied by Maiza et al. (2010) and Madsen et al. (2019). The visual inspection showed several cracks, either longitudinal or map-cracking, and reaction rims were observed around the coarse aggregate particles with exudation of whitish material filling the pores and cracks (Maiza et al., 2010; Madsen et al., 2019). The coarse aggregate corresponds to crushed basalts and the fine aggregate is natural sand composed of quartz, siliceous sandstone, ferruginous sandstone and chalcedony (Maiza et al., 2010; Madsen et al., 2019).

The petrographic examination of the aggregate revealed the presence of partially albitized subhedral plagioclase phenocrysts in a matrix composed of: (1) clinopyroxenes partially altered and associated with opaque minerals; (2) clay minerals (e.g. smectite) in some sectors; (3) localized vitreous matrix (Madsen et al., 2019).

The results of the petrographic examination of the cores are summarized in Table 3.1.

Table 3.1. Summary of the petrographic characteristics of the concrete pavement in Curuzú Cuatiá city.

	Aggregates		Cement paste
	Coarse	Fine	
Polarizing microscope (Maiza et al., 2010)	- Abundant reaction rims - reaction rims in the basalts are not very evident (Madsen et al., 2019) - Basalt particles cracked - matrix of the particles of basalts is heavily devitrified generating clay minerals (e.g. montmorillonite) - whitish area with abundant cryptocrystalline silica	- reaction rims - siliceous sandstone with reaction rims, corroded edges and development of important cracks	- Intense cracking - masked by the presence of neoformation materials (e.g. ettringite and cryptocrystalline silica) - clasts of siliceous sandstones, quartz and cavities partially filled with neoformation materials - Abundant carbonates, sulphates, cryptocrystalline silica and amorphous material - The peripheral areas with degradation phenomena
SEM Madsen et al. (2019)	- presence of gel products in the cement paste-aggregate interface and in voids with calcium silicates (probably hydrated) and with smaller amounts of sodium and potassium - lamellar to fibrous crystalline products arranged radially composed of calcium, sodium and potassium silicates and with minor amounts of aluminium	- a thin layer of reaction material in the cement paste-fine aggregate interface composed mainly of calcium silicates	- cement paste with low carbonation and moderate microcracking and some of them filled with ettringite - voids are partially or filled with ettringite.

Maiza et al. (2010) concluded that despite having signs of ASR in the fine aggregates (e.g. particles of siliceous sandstone with cryptocrystalline silica and chalcedony) this does not constitute a problem for the structural integrity of the concrete. However, they suggested that the basaltic coarse aggregates, together with the alkalis present in the cement, are capable of producing deleterious phenomena causing serious structural damage to the concrete.

The authors also identified the presence of secondary products in the concrete, i.e. ettringite, amorphous to poorly crystallized silica and aluminosilicates (zeolites). Madsen et al. (2019) considered that concrete pavement has good physical characteristics. They concluded that the use of basaltic aggregates together with the fine aggregate, contributed to the development of the reaction and cracking in the structure.

(4) Concrete pavement of the airport of the city of Corrientes

The last case consists of concrete pavement at the airport of the city of Corrientes. This case was also studied by Maiza et al. (2010) and Madsen et al. (2019). The pavement studied by Maiza et al. (2010) links the aircraft parking with the runway. Madsen et al. (2019) refer to two pavement concrete slabs:

- the original slab was manufactured with natural gravel as coarse aggregates, and
- the repair slabs containing basaltic aggregates.

The visual inspection of the concrete cores showed (Maiza et al., 2010; Madsen et al., 2019):

- (1) cracks with map-like distribution and longitudinal cracks in some sectors,
- (2) some of the cracks are filled with a whitish exudation material;
- (3) the presence of holes is scarce;
- (4) there are no signs of segregation;
- (5) the paste is carbonated;
- (6) the air voids are partially or filled with ettringite, and
- (7) reaction rims are visible around the coarse aggregate particles associated with whitish reaction products.

The coarse aggregate is composed of crushed basaltic rocks and the fine aggregate is natural sand with quartz, chalcedony, siliceous and ferruginous sandstones (Maiza et al., 2010; Madsen et al., 2019). Even though the coarse aggregate has been considered a basalt (s.l.), the TAS diagram classified the rock as an andesitic basalt, which indicates a higher SiO₂

content in the rock (e.g. 55.19%) when compared to basalts (s.s.) that range between 45 and 52 wt% of SiO₂ (Le Maitre et al., 2002).

The petrographic examination showed that the aggregate used in the pavement studied by Madsen et al. (2019) is very similar to that of the *concrete pavement from Curuzú Cuatiá*. Once again, partially albitized subhedral plagioclase phenocrysts were identified but this time with smaller amounts of opaque minerals. The matrix included: (1) fresh sanidine crystals; (2) some microcrystalline quartz; (3) quartz associated with adularia; (4) localized vitreous matrix. The presence of clay minerals (e.g. smectite) was only detected by the XRD method (Madsen et al., 2019).

Table 3.2 summarizes the petrographic characteristics of the concrete pavement in the airport.

Table 3.2. Summary of the petrographic characteristics of the concrete pavement in the airport.

	Aggregates		Cement paste
	Coarse	Fine	
Polarizing microscope (Maiza et al., 2010)	- the matrix of basalt particles is composed of smectite together with opaque minerals and sometimes with microcrystalline quartz (Madsen et al., 2019) - reaction rims in the periphery of some aggregates - The reaction rims are composed of iron oxides with an outer rim of cryptocrystalline silica - some aggregates are debonded - the exterior of some basaltic particles composed of ettringite and cryptocrystalline silica	- some particles of quartz are covered by cryptocrystalline silica	- abundant ettringite with calcite - presence of neoformation materials (e.g. ettringite and cryptocrystalline silica) in air voids, empty spaces and cracks
SEM (Madsen et al., 2019)	- aggregates with scarce reaction rims - presence of a whitish material associated with reaction rims with a massive appearance and cracked - some cracks inside the aggregate are filled with a cracked fine-grained material. On both sides of the crack, the material is composed of calcium silicate with minor amounts of aluminium, iron, sodium and potassium. Inside the crack, the material has the same composition but with lower iron content and higher calcium content		- cement paste with strong carbonation and cracking - the air voids are filled with ettringite. - In the paste-aggregate interface a material of similar content to the crack in the aggregate was also identified

Madsen et al. (2019) concluded that the concrete pavement of the airport had some kind of deterioration before ASR appeared; this deterioration favoured the entrance of moisture which led to the development of ASR as a secondary process. The authors affirm that the ASR happened due to the reaction of the mesostasis components and the microcrystalline quartz present in the coarse aggregate matrix and also the chalcedony present in the fine aggregate.

Brazil - Basalts

In Brazil, the first investigations regarding ASR were initiated around the 1980s (Paulon, 1981).

In the Brazilian literature, there are very few cases of ASR in concrete structures associated with volcanic aggregates and they generally resulted in insignificant damage or the reaction stopped and reached some degree of stabilization. Fairbairn (2017) made a list of dams affected by ASR since the 1920s, which included the nature of the aggregate used. In the above list, there are only four cases reported in which basalts were used as aggregates, either as a single coarse aggregate or together with other aggregates in the coarse fraction: (1) Salto do Meio (chimney well) (Pires, 2009); (2) Guaricana (Portella et al., 2012; Fairbairn, 2017); (3) Barra Bonita (Strong et al., 1999) and (4) Porto Colombia. In the first dam, despite having ASR, the coarse aggregate turned out to be a granulite, a metamorphic rock, as reported by Pires (2009) instead of basalt originally reported by Battagin et al. (2009) and Fairbairn (2017). In the second dam (Portella et al., 2012), there is no description of which aggregate is causing the ASR if it is the granite or the basalt. The third dam does not seem to be affected by ASR or if there is any ASR, it is very restricted and isolated (Strong et al., 1997). Some degree of ASR developed in the last dam but the damage has now stabilized.

Salto do Meio (chimney well) hydroelectric power plant dam was studied by Pires (2009). Petrographic examinations conducted on the aggregate and concrete samples extracted from the structure both classified the aggregate as a granulite, a metamorphic rock. In this case, no volcanic rock was used in the construction of this dam.

Guaranica hydroelectric power plant (GHPP) concrete dam is located in the South of Brazil, in Paraná State (Portella et al., 2012). It was constructed in the 1950s (Fairbairn, 2017) and became operational in 1957. This gravity concrete dam is 87-m long and 22-m high. Portella et al. (2012) investigated the dam by using different methodologies and techniques: (1) visual inspection of the concrete structure at the surface and in the galleries; (2) tools and phenolphthalein were used to verify different parameters; (3) SEM/EDS was carried out on selected specimens from concrete cores extracted from the dam; (4) X-ray tomography (CT

scan) was used to evaluate porosity and cracks among others; (5) XRD. The visual inspection of the galleries showed exudations from cracks in the form of stalactites and stalagmites, which confirmed the occurrence of leaching; leaching seemed to have stopped from some cracks due to the presence of clay materials in the water and also by precipitation of calcium carbonate. The cracks also showed a map cracking pattern. The concrete core samples exposed voids and desegregation of the aggregate particles in certain parts of the dam, especially between elevations of 688 and 700 m. The XRD revealed the presence of ettringite, calcite, and other cement paste phases. The petrographic analysis revealed that granite and basalt were the main concrete aggregates and, in terms of mineralogy, quartz, alkali feldspar, pyroxene and muscovite were identified with other minor constituents. The SEM images revealed the presence of cracks, as well as deposits of gel and ettringite in the pores and voids. Despite the presence of ASR gel and ettringite in the dam, the authors concluded that the phenomena responsible for their formation did not seem to be deleterious to the dam.

Barra Bonita dam is located in the Tietê River in the counties of Iguaraçu de Tietê and Barra Bonita (Strong et al., 1997). This dam was constructed in the early 1960s (Battagin et al., 2009) and has a height of 32 m according to the book “100 years of Barra Bonita history – 100 anos de história Barra Bonita” (Mucari, 1983). Since its inauguration, the dam has been facing diverse operational problems, including displacements in three of the four generator units (Strong et al., 1997). CESP at the time elaborated a research program to investigate what was causing this problem. Petrographic analysis was used on concrete cores, extracted from the dam, and on the aggregate (basalt) sampled from the quarry used in the construction, to verify the alkali reactivity. Other methods were also used, like OSIPOV (fragments of aggregate are exposed to a temperature of 1000°C for 1 min if there is any change in the aggregate it is considered potentially reactive) and NBR (Accelerated Mortar Bar Test). According to Strong et al. (1997), the visual inspection, made in 1994, did not find any evidence that the dam was suffering from ASR. Although the petrographic examination of the aggregate, the NBR (expansion = 0.6% at 28-day) and the OSIPOV (fragments of aggregate exposed to a temperature of 1000°C for 1 min, if there is any change in the aggregate it is considered potentially reactive) methods classified the aggregate as potentially reactive. The same authors affirm that the petrographic examination conducted on the concrete samples detected very few significant and isolated signs of the reaction through the presence of alkaline gel, which is suggestive of ASR. The authors concluded that the problem in the dam was not related to any structural movement or ASR.

Porto Colombia dam is located in the Rio Grande between the counties of Planura and Guaíra. According to Galletti et al. (1997), the construction started in 1970 and the dam

became operational in 1973; the dam has a maximum height of 40 m and a total length of 1960 m. Basalt and natural gravel were used as coarse aggregates, while natural sand with 15 to 20% of artificial sand was used as fine aggregate. The authors state that map-cracking was visible in some parts of the dam, in pillars, with a depth of 5 to 50 cm; in some galleries, exudations were observed and also cracks in the power plant with a width of 0.3 to 0.5 mm, possibly all associated with ASR. The authors concluded that the signs of ASR presented in the dam are associated with the basalt aggregate rather than the gravel, which is considered to have low potential reactivity. No differential displacement was noticed in the dam, which lead to the assumption that the ASR would quickly stabilize.

Mizumoto (2009) studied concrete cores incorporating basaltic aggregate from Guadalupe, in Piauí State. However, nothing is mentioned about the structure that was taken. The examination of the concrete cores showed the presence of lumps of whitish gel partially filling voids and cracks and that the aggregate was composed of plagioclase, pyroxene, opaque minerals, apatite, chlorophaeite, quartz and possible devitrified glass. Acicular crystals of ettringite were identified in the voids and a few cracks, but no reaction rims in the interface aggregate/cement paste were found. SEM/EDS showed the predominance of acicular textures, commonly associated with secondary ettringite; the EDS indicated the presence of aluminium, sulfate and calcium, in addition to silica and potassium, showing the possible presence of alkaline calcium silicates. Also, the presence of gel was identified in the concrete core by the calorimetric method. The author concluded that the secondary products present in the pores were predominantly composed of ettringite, which is characteristic of sulfate attack. The different scales of observation and methods used confirmed the coexistence of ettringite and ASR products in the concrete voids.

Iceland – Basalts and rhyolites; gravels

The first proof that ASR was deteriorating concrete in Iceland was detected in concrete houses in 1976 (Ólafsson, 1992; Wigum et al., 2007). Wigum et al. (2007) and Lindgård et al. (2017) mentioned a report from the Icelandic Building Research Institute (IBRI) in 1954, where ASR was considered a possible cause of the damage to Icelandic concrete structures.

Iceland, knowing the problem of ASR, created 1967, a Concrete Committee to investigate the durability of concrete through: (1) field inspections of constructions; (2) research on aggregates and cement; (3) the effect of pozzolans on ASR expansion, as well as (4) temperature and moisture and (5) seawater and freeze/thaw cycles (Wigum et al., 2007; Lindgård et al., 2017). Also, they looked into preventive measures, like the use of pozzolan

cement and non-reactive aggregates. However, these measures were only applied for larger concrete structures during the period between 1961 and 1979, but not in domestic houses (Guðmundsson and Ólafsson, 1996; Guðmundsson and Ólafsson, 2002). At the time, there were mainly two reasons not to use preventive measures in housing. The first one was the increased construction costs associated with the implementation of such special precautions (Ólafsson, 1992). It was also considered that the moisture content was not sufficiently high to cause ASR (Ólafsson, 1992; Lindgård et al., 2017). Ólafsson (1992) also mentioned that there was no knowledge of ASR damage to such constructions anywhere else.

In 1979, the following preventive measures were taken against ASR in new constructions (Ólafsson, 1992; Guðmundsson and Ólafsson, 1996; Guðmundsson and Ólafsson, 1999; Guðmundsson and Ólafsson, 2002):

- Blending silica fume into cement;
- Changing the criteria on reactive material;
- Washing sea-dredged material;
- Limit the use of reactive materials.

Wigum et al. (2007) stated that there was a quick response to the damage caused by ASR, due to the implementation of preventive measures (e.g. silica fume and other pozzolans) proposed after the establishment of the Concrete Committee. Several field surveys were carried out until 1992 (Wigum et al., 2007; Lindgård et al., 2017; Kristjánsson et al., 1979-1987 in Wigum et al., 2007). After 1979, no more ASR concrete damage was identified due to the beneficial effect of silica fume (Guðmundsson and Ólafsson, 1996; Guðmundsson and Ólafsson, 2002).

For the damaged structures, some measures were applied to dry out the houses to stop ASR (Asgeirsson, 1986; Wigum et al., 2007; Lindgård et al., 2017). These included ventilated claddings, mortar-insulation systems, hydrophobic impregnation (Ólafsson, 1992; Wigum et al., 2007), other surface treatments and shotcrete (Lindgård et al., 2017). Asgeirsson (1986) described the following two methods: (1) use of concrete for ventilated sidings often with underlying extra insulation, which is more expensive and interferes with the esthetical appearance of the houses, or (2) use of a surface treatment that prevents absorption and at the same time allows evaporation (e. g. an alcoholic solution of monosilane followed by a thin coating of acrylic paint), being less expensive and more successful than other methods used, but more technically demanding.

It is important to emphasize the weather conditions in Iceland. The country has many annual freeze/thaw cycles, which means that the conditions can change from pouring rain to freezing

conditions within a few hours; this is more frequent, especially in the southern region of the Island (Guðmundsson and Ólafsson, 1996). According to Kristjánsson (1985) and Ólafsson, 1989), the ASR damage in Iceland is not only due to chemical reactions but rather to a combination between chemical reactions and freeze/thaw actions.

In Iceland, the main case studies of ASR-affected concrete structures due to the use of volcanic aggregates are: (1) concrete houses in Reykjavík and the vicinity (Ólafsson, 1992), and (2) Hvalfjörður tunnel (Richardson et al., 1998; Guðmundsson, 2008).

(1) Concrete houses in the Reykjavík region

Between 1961/62 and 1979, severe ASR damage started to appear in several concrete houses (Guðmundsson and Ólafsson, 1996, 1999, 2002; Wigum et al., 2007). The damaged structures included private houses and multi-storey apartment buildings and other buildings in the Reykjavík region (Ólafsson, 1992). The damage was due mainly to the use of a new aggregate source discovered in 1962, that corresponded to sea-dredged basaltic sand from the Hvalfjörður region (Ólafsson, 1992; Lindgård et al., 2017). Ólafsson (1992) states that these aggregates were first subjected to mortar bar tests by the NBRI (National Building Research Institute), which demonstrated that they were considered reactive. These results were then given to the municipal authorities, but no direct action was taken. The aggregates were considered highly reactive due to the high content of rhyolitic material, altered basalt, and the fact that it was a sea-dredged material usually used unwashed (Guðmundsson and Ólafsson, 1996, 1999, 2002).

Over the years, several surveys were carried out (Guðmundsson and Ólafsson, 1996). In 1976, an important report was produced from the examination by the Concrete Research Laboratory in Karlstrup (Denmark) of cores extracted from the first case of ASR in housing foundations (Ólafsson, 1992). The results of the chemical composition of the aggregate particles and the gel present in the concrete are shown in Table 3.3. The same Table gives the chemical composition of the Ordinary Portland Cement (OPC) used at the time (without pozzolans and silica fume). These results point out a high content of CaO in the gel and a high content of SiO₂ in the aggregate particles. Also, the chemical composition of the OPC indicates a high value of Na₂O.

According to Lindgård et al. (2017), several other field surveys followed, more or less every third year until 1992. Guðmundsson and Ólafsson (1996) highlight that in the survey conducted in 1993, an extensive study was made on houses built between 1976 and 1990 and that for the first time, concrete thin sections were examined under the microscope. The gel was

identified in voids and cracks in the concrete of half of the houses constructed in 1977 and one-third of the houses built in 1978. The authors also state that no gel was found in the concrete of houses built after 1979, except in 1981 for which gel was identified in a few isolated voids. Clusters of silica fume were also recognized.

Table 3.3. Chemical composition of the gel, aggregate particles and OPC (Ólafsson, 1992).

Chemical composition of the Ordinary Portland Cement (OPC)		Chemical composition of the aggregate particles		Chemical composition of the gel	
SiO₂	20%	SiO₂	60–73%	SiO₂	70–77%
Al₂O₃	4.3%	Al₂O₃	14–16%	CaO	19–26%
Fe₂O₃	3.5%	Fe₂O₃	10–13%	Na₂O	2–8%
CaO	63.2%			K₂O	0.9–1.6%
Na₂O	1.24%				
K₂O	0.23%				

Guðmundsson and Ólafsson (1999, 2002) refer that one of the surveys was conducted in the case of houses built between 1981 and 1983, where some cores were extracted on which petrographic examination was conducted. It appeared that the OPC contained 5% silica fume and that gel was found only in voids and often closed to rhyolitic or altered basaltic aggregates for two of the houses inspected.

(2) Hvalfjörður tunnel in western Iceland

The tunnel is 5.8 km long, in which about 4 km lie beneath the seabed (Guðmundsson, 2008). Construction started in 1996 and was completed in 1998. One particularity of this tunnel is that it was built near a geothermally active environment where water temperature reaches 58°C and salinity can go up to values of 2000 ppm chlorine (Richardson et al., 1998).

Shotcrete is part of the permanent rock support. Shotcrete layers of about 40 to 80 mm in thickness were applied mostly on the roof sections, while 100 to 150 mm thick layers of fiber reinforced shotcrete were applied in other areas (e.g. heavily jointed rock, clay-filled dykes, fault zones (Guðmundsson, 2008).

According to Guðmundsson (2008), ASR was found in shotcrete after 10 years of service, mostly as gel deposits in voids not connected to cracks; gel was also found in cracks crossing aggregate particles. Different surveys were conducted in 2003, 2005 and 2006, where visual

inspection and petrographic examination combined with SEM studies (to know the composition of the gel) were performed. Table 3.4 presents a summary of these results.

In the project phase of the tunnel, different sources of aggregates were evaluated through AMBT, according to ASTM C-1260, performed either in Iceland or in the UK; a detailed petrographic examination was also conducted on the bars (Richardson et al., 1998). An innocuous mix of aggregate materials was finally selected for the shotcrete, one from natural gravel and crushed rock (e.g. altered basalt, basalt, fresh basaltic glass, altered gabbro and a minor quantity of rhyolite) and the other for the fine aggregate – a sea dredged sand (e.g. fresh and altered basaltic glass, basalt, altered basalt). The shotcrete mix also specified a w/c of 0.41, a cement type CEM II/A-M 42.5R and an admixture wr/sp cement Fly 92M 1.5%. The cement used contained 7.5% silica fume (Guðmundsson, 2008).

Table 3.4. Results of the surveys conducted in 2003, 2005 and 2006 on the shotcrete of the Hvalfjörður Tunnel (Guðmundsson, 2008).

	2003	2005	2006
Visual inspection/Optical microscope	Shotcrete from the geothermal areas: - Gel found in voids not connected with cracks; - Occasionally gel is found in cracks that could be traced to cracked aggregates.	In general, shotcrete in good conditions: - Solid; - No visual evidence of ASR. Shotcrete with surface net cracks: - Cracks penetrate the shotcrete; - Cracked aggregates found - Usually sedimentary rocks cracked - Solid basaltic aggregates found in connection with the cracks	Shotcrete from areas with net cracks: - Gel in voids; - Gel in cracked aggregates - Gel in large cracks that penetrate far in the shotcrete
	Gel associated with cracked aggregate: - Gel with high calcium content and low alkali content; - Gel with sodium and potassium is found next to the basaltic glass.		
SEM	Gel on crack walls: - 3 cm depth from the surface: gel crystallized and made up of calcium carbonate and without silica - Close to the surface: gel brownish in colour		
	Gel in voids not connected with any crack: - Gel with high calcium (close to basaltic or rhyolitic aggregate) - Gel with low calcium but high in silica (far from basaltic or rhyolitic aggregate)		

Guðmundsson (2008) concluded that despite the gel formation, the structure is in good condition and not affected by ASR. Damage due to expansion is considered very limited and

it is assumed that the apparent ASR found in the shotcrete is due to the accelerator used, which contributed alkalis to the mix ($\text{Na}_2\text{O}_{\text{eq}}$ content of about 2.3 kg/m^3). The author presumed that the accelerator is the major source of alkalis and silica.

Japan – Andesites

The ASR found in concrete structures in Japan has been related mainly to the use of andesite and chert aggregates (Yamada and Miyagawa, 2017).

In the book published by Swamy (1992), Nishibayashi et al. (1992) show different examples of Japanese concrete structure types that developed cracking due to ASR and that frequently used andesite coarse aggregates. Some of those structures include: (1) piers; (2) abutments; (3) staircases; (4) sea protection works and (5) retaining walls.

Yamada and Miyagawa (2017) reported other concrete structures affected by ASR due to the use of volcanic aggregates:

- Breakwater elements in Otaru port (Western Hokkaido) (1899): it was used andesitic rocks as aggregates and volcanic ash – ASR gel was identified but no serious damage was detected. Katayama and Sakai (1998) state that signs of ASR were only identified by petrographic examination.
- Railway concrete bridge: highly-reactive andesite aggregate was used. A petrographic examination showed the presence of opaline veins accompanying cristobalite in the andesite.

Okuyama and Torii (2008), Torii et al. (2008), and Sato et al. (2009) also report that there are several Highway Bridges in Noto Expressway (Hokkaido) affected by ASR due to the use of local andesite containing cristobalite and volcanic glass.

In Japan, there are several cases of concrete structures affected by ASR, one interesting case corresponds to a water intake tower from a dam in *Hokuriku*.

Water Intake Tower from a dam located in Hokuriku District (Torii et al., 2016)

The intake tower is located at a dam in the upstream region of the Jouganji River. The tower is a Steel Reinforced Concrete (SRC) structure with a connecting bridge to the mountainside. The structure has an elevation of 1090.7 m above sea level and a height of 63 m. In the cross-section, there is a water intake gate to the lakeside and a solid wall on the mountainside.

After 15/20 years of service, a displacement of 40 mm between the tower and the connecting bridge was measured. The structure was also found leaning towards the lake, from the elevation of 1065 m, and with associated expansion.

The aggregates used in the construction were gravels from the Jouganji River. Petrographic examination showed the presence of granites, andesites and lower amounts of basalts. Both andesite and basalt contained volcanic glass and cristobalite, although opal and tridymite were also identified in the andesite. The authors identified cristobalite and/or tridymite, opal and volcanic glass as the reactive material in the andesite. A survey conducted on bridges and buildings that used this river gravel showed that severe ASR occurred in all of them, even after 2010. This is considered the most reactive volcanic gravel in Japan. This gravel was also submitted to the chemical (according to the Japanese standard – JIS 1145) and mortar bar methods (ASTM C 1260) to evaluate their reactivity; they were classified as not innocuous and deleterious (Expansion 14 days: 0.720%), respectively.

Investigations were conducted in the intake tower to find out the reason for this deformation. Several concrete cores were extracted at different elevations (EL 1070 and EL 1060 m), from: (1) the inside of the mountainside; (2) outside the mountainside, and (3) inside the lakeside. Residual expansion tests were performed on the cores in accordance with the JCI DD2 method. According to this method, drilled cores are cured in a moist chamber with a temperature of 40°C and humidity of about 95%. Cores with an ultimate expansion of not less than 0.05% at 91 days are considered deleterious (Nomura and Torii, 2006). The results point out that there is a slight expansion trend at both EL 1070 m and EL1060 m.

The visual inspection showed extensive map cracking on the interior and exterior wall surfaces of the tower. The cracks were about 0.2 mm in width.

The concrete from the elevations of 1035, 1047, 1060, 1070 and 1087 m was investigated through SEM/EDS. The presence of gel was confirmed in all of the above samples. Examination under the polarizing microscope confirmed that the andesite was causing the formation of ASR gel in the cracks.

The authors concluded that the deformation of the intake tower was caused by differences in ASR expansion due to differences in environmental conditions (e.g. the mountainside wall has more exposure to sunlight) and structural conditions. Some countermeasures and repairs were applied, like the reinforcement of the structure by using a prestressed concrete anchor.

Portugal – Basalts (s.l.)

The first case of ASR in Portugal was detected around 1980, on the Pracana dam, and involved aggregates mainly composed of quartzitic and metapellitic rocks (Silva, 1992). Since then, many other structures are affected by ASR in Portugal, but only one is related to volcanic aggregates. According to Reis et al. (1996), an airport concrete pavement, located on Santa

Maria Island, in Azores Archipelago, was found to be affected by ASR due to volcanic aggregates. In the scope of the ReAVA project, other studies were conducted on the same airport pavement mainly by Fernandes et al. (2015) and Medeiros et al. (2014a, 2015a and b).

Airport concrete pavement

The airport was constructed in the 1950s, using normal Portland cement and basaltic aggregates from a nearby quarry (Reis et al., 1996).

In 1986, several cracks started to appear in concrete slabs, which led to severe degradation of the concrete runway. A study conducted by LNEC in 1989 identified the presence of map cracking and longitudinal cracks along the concrete slabs, with exudations filling some of those cracks. Samples were collected from the quarry and concrete cores from different locations on the concrete pavement. These were subjected to the following test methods: (1) petrographic examination of the basalt; (2) physical characterization; (3) XRD; (4) SEM/EDS; (5) chemical analysis and (6) accelerated expansion tests (Reis et al., 1996). Table 3.5. show the results of the tests.

Reis et al. (1996) state that the results obtained from the study on the airport concrete pavement led to the conclusion that the deterioration is due to a complex process that involved mainly the occurrence of expansive ASR associated with the degree of alteration of the basaltic aggregates. Also, the same authors refer that the progression of the expansive phenomenon might be due to the combination of the: (1) water absorption by the montmorillonites and zeolites and the chemical attack by sulphates from the seawater carried by the rain and the wind.

In 2013, another study was done on the concrete pavement through the ReAVA project (*Characterization of potential reactivity of the volcanic aggregates from the Azores Archipelago: implications on the durability of concrete structures*), from which a report and some conference papers were produced (e.g. Medeiros et al., 2014a; Medeiros et al., 2014b, Fernandes et al., 2015; Medeiros et al., 2015; Medeiros et al., 2016).

Also, within the same project, some samples were collected from the quarry that was used in the construction of the pavement, to perform a petrographic examination and laboratory tests. The quarry is no longer active and is formed by a thick deposit of subaerial basaltic lava flows with some degree of alteration (Medeiros et al., 2014a and 2014b); the rock is chemically classified as basanite (Medeiros et al., 2014a and 2014b, Medeiros et al., 2015a and 2015b). The petrographic examination did not reveal any volcanic glass in the aggregate used, although it could be present in other sections of the quarry (Medeiros et al., 2014a); the mortar

bar test results (ASTM C 1260, 2014) indicated that the aggregate was considered non-reactive (Medeiros et al., 2016).

Table 3.5. Results of the study conducted by LNEC on the basaltic aggregate and concrete cores from the airport pavement (Reis et al., 1996).

	Petrographic examination	XRD	ASTM C 289 Chemical method
Basaltic aggregate	<i>Phenocrysts:</i> - olivine, - pyroxene, - alkali feldspar, - feldspathoid (nepheline) <i>Matrix:</i> - plagioclase, - pyroxene, - opaque minerals, - olivine, - volcanic glass zeolites in pores and cracks	- montmorillonite - the same minerals as in the petrographic examination - magnetite - serpentine	From the 3 samples with different grades of alteration, the test provided positive for the most altered sample
	Visual inspection	XRD and SEM/EDS	Accelerated expansion test
Concrete cores	- Alteration rims around some coarser aggregates - White fine deposits in the interface aggregate/cement - Very porous concrete Fine cracking, especially along the interfaces aggregate/cement	<i>Carbonates:</i> - Interface aggregate/cement - Pores - Microcracks <i>Reaction products with aluminosilicate of calcium mainly sodic</i> <i>Ettringite:</i> - Interface aggregate/cement - Small spaces in the cement paste <i>High amount of sodium in concrete samples</i>	Cores conserved in NaCl at 50 °C with no signs of reactivity

As part of the study of the airport concrete pavement, some concrete cores were drilled from the runway pavement and a petrographic examination was conducted. Some of the concrete cores showed a white deposit lining crack walls and a white rim surrounding the coarser aggregate particles. Additional work was conducted using the SEM/EDS and EMPA (Fernandes et al., 2015). Table 3.6. shows the results of the study of the concrete pavement in the scope of the ReAVA project.

According to Fernandes et al. (2015), the composition of the fibrous material, that occur in the interface aggregate-cement paste, suggests a transitional material between typical chlorite, smectite (e.g. montmorillonite) and zeolite. The authors concluded that this fibrous material,

with variable Ca contents, might have been the result of the reaction occurring between the cement paste and the volcanic glass, being the first one contributing to Ca.

Table 3.6. Results of the study of the concrete cores from the airport pavement and aggregates from an old quarry of Santa Maria Island (Fernandes et al., 2015; Medeiros et al., 2014a, 2015a and b and 2016).

	Aggregates	Concrete cores
Petrographic examination	Phenocrysts: - Olivine with iddingsitized rims, - clinopyroxene, - plagioclase Matrix: - plagioclase, - pyroxene, - opaque minerals - olivine Presence of zeolites	Aggregate particles: - pyroxene - olivine with rims of alteration - rare plagioclase - volcanic glass in the groundmass (either beige to light brown or dark brown) either in the coarse and in the sand fraction - layers of rims of orange fibrous needle-shaped crystals, probably clay minerals. - rare cracks - fibrous minerals in interface aggregate-cement paste Cement paste <i>Textural characteristics:</i> - cracked, - areas with feather-like crystals. <i>Cracks:</i> - Abundant - Randomly-distributed - Similar to map-cracking or desiccation cracks in clay minerals - Some with fibrous minerals <i>Voids:</i> - with fibrous minerals
	SEM/EDS and EMPA	Volcanic glass: - light-coloured glass smooth and uniform (higher content in CaO and FeO and lower content in SiO ₂ and Al ₂ O ₃) - dark glass showed in some particle's crystallites - Si and Al; - low Ca content - very low K, Na, Fe and Mg contents Interface aggregate-cement paste: - Si, Al and Ca - low Mg - very low Na, Fe and K Cement paste: - composed by Si; - low content of Al; - very low content of Ca, Na and Mg

Also, the gel formed contains high Si, variable Ca and low alkali contents. One particularity of the composition of the gel analyzed in this study is that the Al content is somewhat high when compared to the composition of an ASR gel usually formed by siliceous rocks. The authors thus assumed that a different product may have been formed. The cement paste also

appeared cracked and depleted in CaO (e.g. EDS) and agglomerates of acicular crystals within the cement paste seemed to be replacing the cement paste itself.

Turkey (Izmir) – Rhyolite

The first case of ASR damage in Turkey was found in 1995 during the routine inspection of six highway bridges by local engineers (Andiç-Çakır et al., 2012; Fernandes et al., 2017). Before the first case was discovered in 1995, early documentation from 1975 reported that 30% of Turkish concrete aggregates used in some dams were susceptible to ASR (Kocacitak, 1975).

Six highway bridges of Naldöken, Turgutlu, Buca, Hilal2, Halkapınar and Turan

The six highway bridges (Naldoken, Turgutlu, Buca, Hilal 2, Halkapınar and Turan) are located in the vicinity of Izmir and were built from the mid-eighties to the mid-nineties (Andiç-Çakır et al., 2012). Extensive cracking was identified in the decks, piers and abutments of all the above structures (Andiç-Çakır et al., 2012; Fernandes et al., 2017).

The aggregates used in the construction of the bridges included local sand and gravel from the Gediz and Nif rivers and crushed limestone aggregates; it is known that the alkali content of the cement at the time was 0.8 to 1.0% of Na₂Oeq. (Katayama, 2000).

Katayama (2000) performed a detailed petrographic examination of concrete cores extracted from the bridges together with local sand-gravel and crushed aggregates used in the construction of the concrete structures. The author also used AMBT and an accelerated concrete core expansion test. The petrographic examination showed that the sand-gravel aggregates are composed of glassy rhyolite and dacite, andesite, rhyolitic tuff, radiolarian limestone and chert, phyllite and quartz mica schist. The glassy rhyolite and dacite are present in all of the bridges analyzed and the radiolarian limestone and chert in only one. The XRD analysis of the rhyolite detected the presence of cristobalite with a marked pessimum proportion (10%).

The ASR in the field was considered of moderate level for one bridge more than 5 years old and severe for the bridges more than 7-8 years old. In the petrographic examination, ASR was classified as slight for the one-year-old structure and severe in the case of the 5 and 7-8-year-old structures are considered moderate for the other bridges examined. The author shows the following signs of ASR in the different bridges: (1) a reacted and dissolved glassy rhyolite in the Turgutlu bridge; (2) a pop-out with exuding gel in Hilal 2 bridge; (3) a rimmed glassy rhyolite in Naldoken bridge, and (4) cracked glassy rhyolite in Halkapınar bridge.

Regarding the AMBT method (similar to ASTM C1260), the author realized that pure crushed limestone aggregates (coarse and fine) were innocuous (expansion less than 0.03%), while the sand and gravel aggregates tested as deleterious with expansions ranging from 0.18% to 0.51% at 14 days, the most reactive aggregate containing more than 10% of glassy rhyolite and dacite. For the accelerated concrete core expansion test method, the cores were wrapped to keep moisture and stored in a dry oven for 2 hours at a temperature of 80°C and then immersed in 1M NaOH solution at 80°C to monitor expansion until 28 days. The results gave expansions ranging from 0.15 to 0.35% at 14 days.

The author concluded that the glassy rhyolite was the one causing the ASR problems and emphasized that is important to combine different methods to evaluate the presence of ASR.

More recently, Andiç-Çakır et al. (2012) made an additional study on one of the concrete bridges investigated by Katayama (2000) by using EDS analysis. The authors verified that the residual ASR gel present in the reacted rhyolite and siliceous limestone particles presented an increase in CaO content with decreasing alkali content. The authors also highlighted the presence of ettringite inside the air voids and cracks around the aggregate particles.

United States of America, New Mexico (Albuquerque) – Rhyolite to andesite

Lomas Boulevard is located in Albuquerque, New Mexico. It was built in 1992 and a part of the road corresponds to a 155m-long experimental concrete pavement where different preventive measures against ASR were evaluated by the New Mexico State Highway and Transportation Department (Tremblay et al., 2012). According to Folliard et al. (2006) and Tremblay et al. (2012), eleven different concrete mixtures incorporating highly reactive natural gravel aggregates from two sources (e.g. Placitas and Shakespeare pits) were used in combination with Class F/C fly ashes and lithium compounds; two control sections were made for comparison. The cement used had an alkali content of 0.55 Na₂O_{eq} (Stark et al., 1993) and the ratio of the water-cementitious material (w/cm) was generally around 0.40 (Folliard et al., 2006). Five of the eleven mixes contained fly ash at a nominal replacement level of 20% (Folliard et al., 2006; Tremblay et al., 2012). The fly ash came from different sources: (1) the class F fly ash came from the Cholla Generating Station in Phoenix; (2) the class C fly ash came from the Tolk Generating Station in the Texas Panhandle; (3) in the 50-50 blend of class F and class C fly ashes, the “F ash” came from the Escalante Generating Station. Regarding lithium, it was added as a dry powder of lithium hydroxide monohydrate (LiOH.H₂O), with a dosage of 0.5% or 1.0 percent by mass of portland cement. The Lomar admixture consisted of a lithium-bearing high-range water-reducing admixture (Folliard et al., 2006). The control

sections were done without any fly ash or LiOH (Stark et al., 1993). The natural gravels used contained some proportions (< 25%) of rhyolite to andesite and are considered highly reactive (Stark et al., 1993; Tremblay et al., 2012). According to Stark et al. (1993), the Albuquerque aggregates gave an accelerated mortar bar expansion of 0.867% at 14-days. Table 3.7 summarizes the mixtures used in the experimental pavement.

Table 3.7. Summary of Mixtures Used in Lomas Boulevard Experimental Pavement (Folliard et al., 2006).

Aggregates from Shakespeare pit		Aggregates from Placitas pit	
Mix n°	Preventive measure	Mix n°	Preventive measure
1	1.0% LiOH	7	Blend of Class F and C Fly Ash
2	0.5% LiOH	8	Class F Fly Ash
3	Lomar™ Admixture	9	None (Control)
4	Class F Fly Ash	10	1.00% LiOH
5	Class C Fly Ash	11	Class C Fly Ash
6	None (Control)		

Tremblay et al. (2012) made a condition survey for each section and three to four cores were extracted for petrographic examination (DRI determination), GPT and mechanical testing in the laboratory. All concrete sections displayed some cracking but the sections with lithium (0.5%, 1.0% and Lomar™ admixture) and Class F fly ash were the ones presenting the best condition with only minor visible cracking. The petrographic examination revealed that the aggregates contain large proportions of rhyolite to andesite (43% for Shakespeare and 59% for Placitas). The DRI values ranged from 101 to 695, which indicates a degree of damage from low to moderate-severe; the highest values were obtained for the control (695) and the Class C fly ash (625) concretes incorporating the Shakespeare aggregate. The authors determined that the concrete from the mixtures n° 5 and n° 6 were the ones with the highest degree of damage and those that incorporated lithium (n° 1, 2, 3 and 10) and class F fly ash (n° 4 and 11) showed the lowest degree of damage. In general, all cores presented internal cracking in several coarse aggregate particles. The high DRI results obtained from cores n° 5 and 6 are due to the presence of higher proportions of cracks with reaction products both in the aggregate particles and in the cement paste. Table 3.8 summarizes the results obtained by the petrographic examination (DRI) and the GPT methods.

At the end of about 16 years in service, the authors concluded that the use of lithium-based products (LiOH 1.0 and 0.5%, LomarTM admixture) and about 20% class F fly ash was effective in reducing/controlling expansion and cracking in concrete pavement sections with highly-reactive aggregate from Shakespeare pit. However, in the case of the specimens incorporating the Placitas aggregates, the authors indicated that it was not possible to conclude about the efficacy of the preventive measures applied to sections n° 7, 8, 9, 10 and 11 due to the low degree of internal damage obtained by the DRI on the control specimen (n° 9).

Table 3.8. Petrographic examination results of the concrete cores from the experimental Pavement

Petrographic examination of the polished sections of the concrete cores	DRI Method	Gel Pat test method
<i>Aggregates:</i> - majority: composed by rhyolite to andesite - quartzite, quartzitic sandstone, siltstone, granite - minor amount: limestone	DRI values range: 101-695 (Low to moderate-severe). <i>Low degree of damage:</i> Mix. n° 1, 2, 3, 4, 10, 11 <i>High degree of damage:</i> Mix. n° 5 and 6	Significant amounts of gel are associated with volcanic rock types, i.e. dacites, rhyolites, latite and some andesites

3.1.1 Volcanic aggregates considered potentially reactive by different test methods

Several examples of volcanic aggregates that tested potentially reactive or reactive through different test methods are described in this section. These aggregates included mainly andesites, basalts and rhyolites studied by different researchers from several countries such as Argentina, Australia, Brazil, Czech Republic, Iceland, Japan, Turkey and the United States of America. These aggregates were subjected to different test methods mentioned in the different reports and articles consulted and presented here. Some of the methods comprised the petrographic examination and the mortar bar test with or without acceleration (ASTM C 1260 or ASTM C 227). The CPT is less performed when compared to the mortar bar test. Petrography is always done by a polarizing microscope and sometimes is complemented by SEM/EDS or/and EMPA and also XRD. In some studies, the results of the geochemical analysis are shown and only in a few cases, the phosphoric acid method is mentioned and performed.

Argentina-Basalts and rhyolites

In Argentina, the results of several studies on ASR have been published, with a special focus on volcanic rocks, either on coarse or fine aggregates (Batic et al., 1994; Maiza et al., 1995; Marfil and Maiza, 1996; Maiza and Marfil, 1998; Marfil et al., 1998; Maiza and Marfil,

2003; Maiza et al., 2003; Maiza and Marfil, 2004; Maiza et al., 2005; Marfil et al., 2005; Marfil and Maiza, 2006; Maiza et al., 2006a; Maiza et al., 2006b; Priano et al., 2006; Maiza and Marfil, 2008; Maiza et al., 2008; Milanesi, 2008; Milanesi et al., 2008; Priano et al., 2009; Maiza et al., 2010; Marfil et al., 2010; Rocco et al., 2012a; Rocco et al., 2012b; Marfil et al., 2013; Rocco et al., 2016; Milanesi et al., 2018; Madsen et al., 2019). Basalts were found to be the main issue in many cases (Batic et al., 1994; Maiza et al., 1995; Marfil and Maiza, 1996; Maiza and Marfil, 1998; Marfil et al., 1998; Maiza and Marfil, 2004; Maiza et al., 2005; Marfil et al., 2005; Maiza et al., 2006a; Maiza et al., 2006b; Priano et al., 2006; Maiza and Marfil, 2008; Maiza et al., 2008; Milanesi, 2008; Milanesi et al., 2008; Maiza et al., 2010; Marfil et al., 2010; Priano et al., 2012; Rocco et al., 2012a; Rocco et al., 2012b; Marfil et al., 2013; Milanesi et al., 2016; Berezosky et al., 2015; Rocco et al., 2016; Madsen et al., 2019). There are also some works published for rhyolitic (Maiza and Marfil, 2003; Maiza et al., 2003; Maiza and Marfil, 2004; Marfil and Maiza, 2006; Maiza et al., 2006b; Priano et al., 2006; Maiza et al., 2008) and andesitic rocks (Maiza et al., 2008; Berezosky et al., 2015; Milanesi et al., 2018; Madsen et al., 2019) from the point of view of ASR but in less quantity when compared to basalts.

Basalts are widely distributed in Argentina, particularly in the regions of Mesopotamia, the Andes, the Central area (e.g. Cordoba), and Patagonia (Batic et al., 1994; Maiza et al., 1995). The basalts belong either to the tholeiitic or the alkaline series (Batic et al., 1994; Acevedo, 2016), the tholeiitic one being more referenced in several works (Batic et al., 1994, Marfil et al., 2013).

Batic et al. (1994) investigated the potential reactivity of basalts through mortar bar test (NBRI) and petrographic examination of the mortar bars. Two samples of aggregates were investigated, one from Piedra del Aguila zone (Patagonia) and the other from a zone near Yacyretá (Río Negro Province). The petrographic examination of the rocks showed that Piedra del Aguila presents slight signs of alteration and the texture varies from intergranular-subophitic to intersertal. The other basalt showed intergranular groundmass with abundant montmorillonite, chlorite and zeolite; a small amount of volcanic glass partially devitrified (palagonite) was also observed. The mortar bar test (ASTM C 227) was used with both aggregates and with low (M-2: Piedra del Aguila; M-4: Yacyretá) and high alkali cement (M-1: Piedra del Aguila; M-3: Yacyretá). The results showed that only the basalt from Yacyretá gave high expansions (0.331% -14 days) when the high-alkali cement was used. The M-4 bars increased in expansion by more than 300% between 14 and 28 days, with 0.171% of expansion at the end of 28 days. The petrographic examination of mortar bar M-3 showed cracks and signs of reaction inside aggregate particles, air voids partially filled by amorphous material, and some cracks filled with zeolites; clay minerals (montmorillonite) were also

observed and the paste showed destroyed. The mortar bar M-4 presented cracks and air voids filled with zeolites. The authors concluded that: (1) the mortar bar test showed the same distress as the concrete structures presenting ASR, (2) besides volcanic glass, smectite has contributed to ASR; (3) zeolite is the main component observed in the reaction products and montmorillonite is the main component observed in reactive basalts.

Maiza et al. (1995) examined basaltic rocks from different locations in Argentina to know their potential reactivity when used as concrete aggregates. The methods used included the mortar bar test (ASTM C 227), AMBT (ASTM C-9 P-214), chemical method (ASTM C 289), XRD and petrographic examination (polarizing microscope). The study included twelve rock samples: Garrapata, Los Cóndores 1, Los Cóndores 2, Comallo, Aguada de Guerra, La Pasarela, Cornallo compacta, Cornallo porosa, Yacyretá 1, Yacyretá 2, Misiones, Yacyretá 3 and La Calera. The petrographic examination showed that some basalts do not contain volcanic glass (La Pasarela, Los Cóndores, Garrapata, Cornallo compacta) while others have in small quantities (Aguada de Guerra, Cornallo porosa, Misiones) or in abundance (Yacyretá). Some samples show evidence of alteration by the process of chloritization (Aguada de Guerra, La Calera, Los Cóndores, Garrapata, Misiones) or by the presence of clay minerals, especially montmorillonite (Aguada de Guerra, Yacyretá, La Calera, Misiones). The presence of clay minerals was confirmed by XRD. The results obtained by the AMBT (ASTM C9 P-214) at 14 days (threshold of 0.10%) considered Yacyretá, Misiones and La Calera potentially reactive with expansions of 0.192%, 0.159% and 0.303% for Yacyretá 1, 2 and 3, respectively, 0.214% for Misiones and 0.403% for La Calera. Also, the results of the chemical method ASTM C -289 indicated high dissolved silica contents for the majority of the rock samples considered potentially reactive in AMBT, with values of 23.0 mg and 57 mg for Yacyretá 1 and 3, respectively, 79.5mg for Misiones and 32 mg for La Calera. As the degree of alteration increases due to the clay minerals present in the rock and due to the presence of volcanic glass in the groundmass, the dissolved silica value increases. The authors assumed that the reactivity of these rocks is due to the presence of volcanic glass and/or clay minerals (montmorillonite).

Marfil and Maiza (1996) studied the mineralogical characteristics of basalts from the Northern of the Macizo of Somuncura, to identify ASR deleterious components. The research included different basaltic rocks: Cerro Mesa, Tte. Maza compact and porous, El Cuy compact and porous, Pajalta (upper basalt, middle basalt, lower basalt, basalt in contact with marl) and Bajada del Sauce. The majority of the rocks showed volcanic glass, some of them displaying devitrification. Also, clay minerals were dominant in these rocks. The petrographic examination of Bajada del Sauce revealed no signs of alteration nor the presence of volcanic glass, either

fresh or altered, and no minerals filling the vesicles of the rock. The authors considered this rock non-reactive, based on petrography only, and the only one suitable for concrete aggregate. Regarding the other rocks, the authors assumed that more tests needed to be conducted, because they are classified as reactive from the point of view of petrography.

Marfil and Maiza (2006) studied the potential reactivity of eleven volcanic samples from Patagonia, mainly through petrography. The results from the petrographic examination were then compared with those obtained in the AMBT (ASTM C 1260) and the chemical method (ASTM C 289). The samples included only rhyolites: Florentino Ameghino, Villegas, Cantera 60; cerro Alto, Sierra Chata red and black, Pajalta, Do Ricardo, Sierra Grande and Sierra Colorada. The presence of volcanic glass was observed in all samples except Florentino Ameghino, which contained a microcrystalline matrix. Most samples showed an intersertal matrix and alteration processes where argillization was the common denominator, followed by zeolitization and silicification. The expansions obtained by the AMBT ranged from 0.026% (Florentino Ameghino) to 0.197% (Cerro Alto) at 14 days. Petrography revealed no glass in the sample Florentino Ameghino, while the matrix of the Cerro Grande sample had a hyalopilitic texture partially recrystallized with alteration processes (argillization). The results of the dissolved silica obtained from the chemical method were mostly in accordance with those of AMBT. The authors considered that the samples classified as deleterious by the standard tests were those containing relict glass, glassy groundmass with some alteration processes and with microcrystalline silica and/or chalcedony. The authors concluded that rhyolitic rocks with entirely recrystallized coarse-grained matrices are not reactive and are suitable for concrete aggregates, which is the case for the Florentino Ameghino and Villegas samples. The authors also concluded that rhyolitic rocks may develop deleterious reactions when they contain fresh and/or altered glass in their groundmasses, as well as alteration minerals resulting from devitrification, such as argillaceous minerals and cryptocrystalline silica.

Maiza et al. (2006b) used petrographic examination and the AMBT method to investigate the potential alkali-reactivity of basaltic and rhyolitic rocks from Patagonia. The investigation included three rhyolites (Camarones, Albistur and Bienvenida), one trachyte (El Cain), one trachybasalt (Meseta de Somún Curá) and eight basalts (Facundo, Huala, Pillahuincó Compacto, Pillahuincó poroso, Ruca Choroi, Cerro Medina, Ing. Jacobacci and Cabecera del Salado); however, the authors recognized that among the basalts, two correspond to trachybasalts (Pillahuincó poroso and Ruca Choroi). A petrographic examination did not reveal any volcanic glass in the rhyolites. The rhyolite Camarones showed a microgranular texture with silicified sectors where quartz forms poikilitic textures. The rhyolite Albistur presented phenocrysts of quartz and sanidine in a microgranular groundmass, with sectors including

chlorite and montmorillonite. The rhyolite Bienvenida revealed phenocrysts of quartz and sanidine partially argilized in a microgranular groundmass with evidence of a perthitic texture. The petrographic examination of trachyte and trachybasalt did not show any reactive minerals or volcanic glass. Petrography did not reveal any volcanic glass in some basalts (Huala, Pillahuincó poroso, Ruca Choroi), but small amounts of scarcely distributed devitrified glass in others (Facundo, Ing. Jacobacci). The basalt Pillahuincó Compacto presented a higher volcanic glass content (relict > 5%), sometimes devitrified, in the groundmass. The basalt Cabecera del Salado was the only one presenting abundant fresh volcanic glass (> 5%) but also devitrified glass with iron oxides, silica and other secondary minerals in some sectors. The basalt Ing. Jacobacci was the only one showing chloritization. The results from the AMBT at 14 days (IRAM 1674) classified only three of the rocks as reactive with expansions of 0.127% for rhyolite Albistur, 0.337% for basalt Pillahuincó Compacto and 0.360% for basalt Cabecera del Salado. The reactivity was found to increase with the amount of volcanic glass, as shown by the basalt Pillahuincó Compacto and basalt Cabecera del Salado. As for the rhyolite Albistur, the authors attributed the reactivity to the presence of montmorillonite but further studies should be done.

Milanesi (2008) studied a basaltic aggregate produced from a quarry near the construction site of concrete pavement on National Road 14. The study included petrographic examination, phosphoric acid test, dissolved silica content determination, and expansion tests (mortar bar and CPT), among others. The aggregate was sent to two laboratories to perform a petrographic examination; however, the results obtained by each laboratory on the same aggregate were quite different. One of the laboratories considered the aggregate non-reactive with no clay minerals and no cryptocrystalline silica, with scarce volcanic glass and devitrified glass (palagonite). The other laboratory considered the aggregate potentially reactive with the presence of variable amounts of fresh and altered volcanic glass, clay minerals (saponite and montmorillonite) and cryptocrystalline silica. The phosphoric acid test detected the presence of cristobalite (1.4%) and tridymite (1.3%). The results obtained for the expansion tests considered the aggregate reactive with expansions of 0.527% for the mortar bar test at 14 days (IRAM 1674) and 0.047% for the CPT at end of the one-year testing period (IRAM 1700). The result of the dissolved silica content (ASTM C 289) gave a result of 38 mg/l, which is higher than the value recommended. According to these results, the author concluded that the presence of cristobalite and tridymite in this tholeiitic basalt is the result of the devitrification of volcanic glass which also leads to the formation of clay minerals. The presence of silica minerals should alert geologists regarding ASR. The CPT results confirmed that the aggregate is moderately reactive, which is coherent with the results from the petrographic examination of

the second laboratory. The authors reported that no apparent correlation existed between the expansions in the CPT and the AMBT. The authors believe that the higher AMBT expansion may be related to the need to crush the aggregate and expose a greater surface of the rock to the attack by the alkalis, which does not occur when basalt is used as a coarse aggregate.

Marfil et al. (2013) studied basaltic aggregates from NE of Argentina to identify deleterious species through petrography and other laboratory tests. The results of the petrography were then compared with the behaviour of these aggregates in structures in service. The authors studied three rock samples from: Yeruá, Curuzú Cuatiá 1 and Curuzú Cuatiá 2. All basalts are tholeiitic and all have in common the presence of volcanic glass and clay minerals due to the alteration of volcanic glass. One of the samples (Curuzú Cuatiá 1) contained cryptocrystalline silica identified by XRD. In two of the rock samples (Curuzú Cuatiá 1 and Curuzú Cuatiá 2), chlorite and celadonite were present both determined by XRD. The results of the AMBT (ASTM C 1260) at the end of 14 days showed all rock samples as potentially reactive with expansions ranging from 0.425% to 0.503%. These aggregates were used in the construction of a section of National Road 127 and of a runway in Corrientes city, where ASR was considered the major cause of deterioration. However, the authors reported that not all concrete made with these materials developed ASR and that even some of them were in perfect condition.

A part of the study by Madsen et al. (2019) had the objective of evaluating the potential reactivity of crushed basalt from two quarries (A and B) of the NE of Argentina. The study comprised petrographic analysis, XRD and laboratory expansion tests (AMBT, CPT and ACPT). The results of the geochemical analysis indicated that rock sample A is a basalt and rock sample B is an andesitic basalt. Under the microscope, both rocks presented intersertal to intergranular texture, while some sectors showed clay minerals and others vitreous groundmass. The clay minerals, smectite, were identified by XRD only in sample A, while its proportion was too low to be detected in sample B. Microcrystalline quartz and quartz associated with adularia were detected only in sample B. The authors emphasized that volcanic glass, determined by modal analysis, showed a value of almost 3% for sample A against only 0.5% for sample B. Considering that dissolved silica values (IRAM 1650) higher than 20 mg classify rocks as potentially reactive, the results showed sample A as potentially reactive (37.0 mg) and sample B as not reactive (7.0 mg). According to the Argentinian standards (IRAM 1674), where 0.10% defines the limit of potential reactivity, the results of the AMBT method at the end of 14 days classified both rocks as potentially reactive with expansions of 0.498% for sample A and 0.207% for sample B. For the CPT method (IRAM 1700), where 0.04% at the end of one year defines the limit of potential reactivity, the results

classified only sample A as potential reactive, with an expansion of 0.089% while an expansion of 0.003% was obtained over the same period for sample B as for the ACPT, both rock samples were classified as non-reactive, with expansion values of 0.037% for sample A and 0.010% for sample B. The Argentinian standard for the ACPT method specifies a limit of 0.04% at 13 weeks to consider the aggregate potentially reactive. The authors concluded that sample A must be classified as potentially reactive and sample B as non-reactive by taking into consideration the results of CPT. The authors also point out that the amount of volcanic glass and probably clay minerals contributed to the potential reactivity of aggregate A. As for aggregate B, the authors considered that the amounts of volcanic glass and clay minerals were very low and the presence of microcrystalline quartz probably contributed to the classification of potential reactivity in the AMBT method.

Australia - Basalt

In Australia, different rock types are used as aggregates, some of them are volcanic rocks. According to the Department for Energy and Mining of the Government of South Australia, the volcanic rocks exploited in this region are: (1) Mesoproterozoic acid volcanic rocks of the Gawler Range Volcanics suite that were used for railway ballast north of Tarcoola, and road aggregate at Kingoonya and the northern Eyre Peninsula, and (2) Quaternary basalt deposits that supply the Lower South-East with aggregate from the Mount Schank and Mount MacIntyre Quarries

(http://www.energymining.sa.gov.au/minerals/mineral_commodities/construction_materials 06-07-2020).

McNally (1998) also reported on the main aggregates and sources that are used in some of the cities in Australia, some of these being of volcanic nature:

- Basalts are used as aggregates and volcanic breccia are used for roadbase in the Sydney region;
- Most of Melbourne's aggregates and roadbase are obtained from basalts from the older Volcanics (east and north of the city) and Younger Volcanics (west and north);
- In Brisbane, the majority of the aggregates are derived from dredged river gravels, but it is complemented with crushed basalts, acid volcanic and other igneous and metamorphic rocks.

In Australia, extensive work was done in the past to investigate ASR in the country. Shayan and Freitag (2017) made a list of the Australian reactive aggregates based on the work done

by Harold Vivian in the 1950s but also through the addition of more reactive aggregates obtained more recently either by the examination of ASR-affected structures or by newer laboratory testing methods. The volcanic aggregates considered reactive are the following: (1) dacite and rhyodacite tuff from New South Wales; (2) rhyolite from Northern Territory; (3) Beerburrum trachyte, ignimbrite/rhyolite and glass-bearing basalt from Queensland; (4) basalt from Tasmania and (5) dacite, rhyodacite from Victoria.

Several volcanic aggregates have been studied from the point of view of alkali-silica reactivity; even basalts have been classified as reactive in different test methods.

Shayan and Quick (1988) found out that basalt from Queensland was considered highly reactive with the presence of 1.6 % of opaline silica. In this study, the authors compared two basaltic aggregates, one from Queensland and another from Victoria. Different test methods were used to investigate these basalts. A petrographic examination of the basalt from Queensland identified a dark glassy groundmass and a colourless isotropic material that rimmed carbonate minerals and a greenish-brown isotropic material. In contrast, the Victorian basalt was less glassy and olivine was showing alteration. SEM and EMPA were used on both aggregates and the dark rim was revealed to be opaline silica and the greenish material clay mineral; the alteration material of the Victorian basalt was recognized as chlorite. The EMPA analysis showed that the opaline silica had a composition of 91.80% of SiO_2 and the volcanic brown glass of 67.32% of SiO_2 . Another method used in this research was the chemical analysis performed on both basalts by XRF; the results obtained showed that the chemical compositions are very similar, the SiO_2 content being higher in the case of the Queensland basalt. The Queensland basalt caused large expansions and cracking in the mortar bar test according to the ASTM C-227 at 38°C and 100% RH (1.74% at 18 weeks), in the AMBT with the bars immersed in 1M NaOH at 80°C and in the CPT similar to the ASTM C-1293. On the other hand, the basalt from Victoria did not show any significant expansion even when the alkali content of the mortar and concrete mixes was increased. The authors concluded that:

- (1) despite bulk compositions, there was significant localized enrichment with silica in the case of the Queensland basalt, which rendered it reactive to alkali hydroxide;
- (2) the Victorian basalt is considered non-reactive even with high-alkali content in the mortar and concrete mixes, which is considered the opposite for Queensland basalt;
- (3) the Queensland basalt should not be used in concrete without performing further investigations of the whole rock source.

Shayan (2004) studied another basalt from Australia that had the same behaviour as the Queensland basalt reported by Shayan and Quick (1988). An electron probe analysis identified a silica-rich glassy phase with a SiO_2 content of 87.8%. The AMBT performed on this basalt gave expansions of about 0.30% at 21 days and 0.8% at 42 days. The mortar bars presented map-cracking and thin sections made from them revealed cracks crossing reacted aggregate particles with connections between some reacted particles. Some of the wider cracks appeared to be filled with ASR products, which was confirmed by EDX spectra. Also, CPT was performed with this basalt, using a concrete alkali content of $7.5 \text{ kg Na}_2\text{O}_{\text{equi.}}/\text{m}^3$; after one year of storage at 40°C and 100% RH, the prisms gave 0.03% of the expansion. Companion concrete prisms cured at 75°C and then stored at 50°C and 100% RH gave an expansion of 0.18% at the end of one year of testing. The author mentioned that when the alkali content was reduced to $5.5 \text{ kg Na}_2\text{O}_{\text{equi.}}/\text{m}^3$, the expansion was very small, even under the same (accelerated) conditions as the above. Shayan (2004) concluded that different basalts can behave differently from the point of view of alkali reactivity. The author categorizes basalt reactivity in terms of its behaviour in the expansion tests:

1. Basalts with insignificant expansion in both AMBT and CPT methods are considered non-reactive;
2. Basalts with significant expansion in both AMBT and CPT methods are considered reactive;
3. Dense glassy basalts with significant expansion in AMBT but very little expansion in CPT are considered non-reactive but can cause a reaction in sand fraction.

Shayan and Quick (1988) and Shayan (2004) assumed that the alkali reactivity of some Australian basalts is related to the presence of glassy/opaline material in those rocks.

Although there are some studies in which basalts were considered reactive, the majority of Australian basalts are reported as non-reactive. Some examples are presented in the work performed by the following researchers: (1) basalts from Western Australia (Shayan et al., 1987; Ross and Shayan, 1986 in Shayan, 2004); (2) basalts from Victoria (Shayan et al., 1988; Shayan et al., 2003; Shayan, 2004). Ross and Shayan (1986 in Shayan, 2004) reported a basalt from Western Australia that contained patches of a glassy phase that expanded a lot in the AMBT.

Brazil - Basalt and rhyolite

In Brazil, the production of crushed volcanic rocks is concentrated in different regions and with different rocks, among others (DNPM, 2015):

- Ceará (phonolites)
- Goiás (basalt)
- Maranhão (basalt)
- Minas Gerais (basalt)
- Mato Grosso do Sul (basalt)
- Mato Grosso (basalt)
- Paraná (basalt and rhyolite)
- Rio Grande do Norte (phonolites)
- Rio Grande do Sul (basalt and rhyolite)
- Santa Catarina (basalt)
- São Paulo (basalt)
- Tocantins (basalt)

Several types of research were conducted to know the potential reactivity of different Brazilian volcanic rocks. In these investigations, several basalts were classified as potentially reactive according to the different methods used.

Volcanic glass, tridymite, cristobalite, devitrified glass (palagonite), chalcedony and opal are among the main reactive components within Brazilian volcanic rocks. In addition, some authors (Couto, 2008; Tiecher et al., 2018) affirm that clay minerals seem to contribute to the occurrence of ASR. Besides these specimens, chlorophaeite is commonly mentioned as a reactive component of basalts in Brazil. It is referenced by different researchers (Hasparyk, 1999; Munhoz and Cincotto, 2008; Couto, 2008; Mizumoto, 2009) and also by the Brazilian standard ABNT NBR 15577-3 (2018), which defines it as: “a mix of clay minerals of magnesium, iron and calcium that presents a greenish to reddish brown colour”. By secondary processes, chlorophaeite replaces olivine, pyroxene and volcanic glass by keeping, their form (e.g. pseudomorph). Chlorophaeite usually occurs in basalts, filling cracks, vesicles and in between the interstitial spaces of plagioclases. According to Jackson (1997), it is a mineraloid related to the chemical composition of chlorite and corresponds to a hydrated silicate of magnesium, iron and calcium; it occurs in tholeiitic basalts filling the spaces between the feldspars, as olivine pseudomorphs, or in veins or pores; Vieira and Oliveira (1997) state that chlorophaeite comes from glass devitrification. A website very used by mineralogists affirms

that it is a material of uncertain status, that was first considered as “possibly a chlorite” (<https://www.mindat.org/min-951.html> - 01-06-20). A recent study by Środoń et al. (2019) however indicates that it is a product of the alteration of volcanic glass.

Hasparyk (1999) carried out an experimental program to evaluate the efficiency of different levels of active silica and rice husk ash in substitution to cement (0, 4, 8, 12 and 15%), by using the expansion of mortar bars (AMBT according to ASTM C 1260) and two types of aggregates: a basalt and a quartzite, both considered reactive. Additional methods were used, such as a petrographic examination of the aggregates and microstructural analysis of the mortar bars by using a stereo binocular microscope and SEM/EDX. Both the optical microscope and the SEM/EDX indicated the basalt to be composed of plagioclase, pyroxene, opaque minerals, chlorophaeite and volcanic glass. The AMBT with no admixtures (0%) classified the basaltic aggregate as reactive with expansions of 0.84% at the end of 14 days of testing, being more reactive than the quartzite with 0.28% of expansion for the same period. The AMBT results indicate that both admixtures were able to reduce significantly the expansion by increasing the percentage of pozzolanic addition. The visual analysis of the mortar bars showed longitudinal cracks and some bending, that start to decrease with the increase of the percentage of the admixtures. In the stereo binocular microscope, the pores appeared filled with white material and a darker rim surrounds some aggregate particles. The SEM/EDX performed on the mortar bars showed that the white material is composed of silico-calcium-alkaline gel with different morphologies (e.g. amorphous or crystalline), being present both in the pores and in the cement/aggregate interfacial zone. Cracks were also present in the gel, in the aggregate particles and within the cement paste and more frequently in the basalt than in the quartzite aggregate, especially within bars with no admixtures. It was noticed that cracking started to decrease with an increasing percentage of pozzolanic admixtures. The gel presented a variable chemical composition depending on the pozzolan content and the aggregate used. The author concluded that: (1) the presence of volcanic glass and chlorophaeite is indicative of reactivity in the basalt studied; (2) the more disorganized and unstable the structure of the minerals present in the aggregates, the more reactive it will be; (3) the reaction that occurs in both aggregates is confirmed to be ASR; (4) the pozzolan addition is effective in reducing expansion, which was visible by a more dense cement paste, with fewer pores and a better adherence in the aggregate/cement paste interfacial zone. The pozzolan content has a great influence on the chemical composition of the gel. In general, the content of $\text{Na}_2\text{O}_{\text{eq}}$ and SiO_2 is reduced while the content of CaO and CaO/SiO_2 increases with increasing admixture content (pozzolan).

Munhoz (2007) and Munhoz and Cincotto (2008) studied a basalt from the Marília region of São Paulo state and a granite mylonite from the Grande Recife region of Pernambuco state, to evaluate their reactivity with or without SCMs. The petrographic examination showed that the basalt contained volcanic glass, chalcedony and chlorophaeite and the granite revealed deformed quartz and microgranular quartz. For the AMBT method, using Portland cement CP V-ARI, the results showed both aggregates as reactive; the basalt gave more expansion than the granite at the end of 14 days of testing, with 0.49% for basalt and 0.25% for granite. All SCMs used (e.g. blast-furnace slag, fly ash, metakaolin and silica fume) contributed to mitigating ASR, some being more efficient than others. The authors concluded that the reactive phases in basalts are vitreous and amorphous material, while they correspond to crystalline phases in the case of granite. According to the AMBT results, it was concluded that these aggregates could be used in construction with cement containing SCMs.

Couto (2008) presented the results of an investigation of several siliceous aggregates commercially used in the State of Goiás and compared them with: (1) aggregates used in case studies of concrete structures affected by ASR, (2) other aggregates used in civil construction of Pernambuco, and (3) a highly-reactive aggregate from Paraná. The author used the following methods: petrographic analysis, ASTM C 1260, ABNT NBR15577-4 and accelerated concrete prism test (ACPT) (ABNT NBR15577-6). Twenty-two aggregate samples were collected; seven of them were basalts with the following code names: BA.1, BA.2, BA.3, BA.4, BA.5, BA.6 and BA.7. The following two types of cement were selected for the laboratory tests: CP II-F-32 (Portland cement with filler- cement A) and CP IV-32 (Portland cement with pozzolan - cement B). All basalts were classified as potentially reactive based on petrographic examination due to the presence of volcanic glass, clay minerals and green chlorophaeite. Sample BA.7 also contained microgranular quartz. The AMBT method was performed in accordance with ASTM C 1260 and ABNT NBR15577-4. The results obtained with cement A, according to ASTM standard, considered reactive the sample BA.7 with 0.61% of expansion and sample BA.5 as potentially reactive with an expansion of 0.28%, both at the end of 14 days. The rest of the samples were considered innocuous with expansions below 0.10%. For the Brazilian standard, samples BA.4, BA.5 and BA.7 were classified as potentially reactive and the rest of the samples as potentially innocuous with expansions below 0.10%. On the other hand, the results obtained with cement B (with pozzolan) were quite different, all basalts being classified as innocuous. The accelerated concrete prism test was performed with cement A, non-reactive sand at a temperature of 60°C and only for basalts BA.3, BA.4 and BA.7 that were considered innocuous by the ACPT. No cracking or signs of deterioration were visible in the concrete prisms at the end of six months of testing. SEM/EDS analyses showed that all

prisms contained ASR products in some of the pores, with a silico-calcium-alkaline composition. The author also emphasized that there was a certain debonding of the aggregate particles from the cement paste in all of the samples analyzed.

Mizumoto (2009) studied the potential alkali-reactivity of six aggregates mainly through petrographic analysis and expansion tests (AMBT and ACPT). Two of the aggregates selected were considered basalts; one came from Andranina in São Paulo State (B1 sample) and the other from Caçu in Goiás State (B2 sample). The petrographic examination showed that, besides the typical mineralogy of basalts (e.g. plagioclase, pyroxene, opaque minerals), both aggregates contained devitrified glass and clay minerals and only B2 aggregate showed fresh volcanic glass. The petrographic analysis classified both of them as potentially reactive. The XRD analyses confirmed the presence of some quartz in both samples, which pointed out the existence of silica in the mesostasis. For the AMBT method (NBR 15577-4), a standard cement ABCP (Associação Brasileira de Cimento Portland - Brazilian Portland Cement Association) with a $\text{Na}_2\text{O}_{\text{eq}}$ content of $0.90 \pm 0.10\%$ was used; the mortar was made with a w/c ratio of 0.47 and graded aggregates (0.30-4.75 mm). Both aggregates were classified as potentially reactive, these basalts having produced the highest expansions of all aggregates selected in this study. Also, basalt B2 induced higher mortar bar expansion than basalt B1. The macroscopic analysis of the mortar bars revealed a flexion of the bars and continuous cracking in both cases. The accelerated concrete prism method (ACPT) (NBR 15577-6) was performed at temperatures of 38 and 58°C. For the 38°C testing series, basalt B1 was considered potentially reactive after nine months of testing, while basalt B2 presented a gradual increasing expansion trend over the last readings; both aggregates were classified as innocuous based on the 58°C testing series. The macroscopic analysis of the concrete specimens exhibited efflorescence in both aggregates. Under the optical microscope, the presence of ettringite was detected in voids of the concrete made with basalt B1, while such deposits were observed in concretes incorporating both basalts under the SEM/EDS. In the case of concrete prisms incorporating B1 basalt tested at both temperatures and for those with B2 basalt at 58°C, SEM/EDS observations revealed very few crystalline structures composed of calcium and silica in pores, besides the presence of silico-calco-alkaline. Some of the author's conclusions about their work are summarized below:

- (1) The basalts B1 and B2 were considered potentially reactive in the AMBT method;
- (2) Regarding the CPT, a relationship was found between the expansive behaviour and the weight variation of the test prisms. This was proven by both samples B1 and B2 that presented weight reductions at $T = 58^\circ\text{C}$ and a consequent decrease in the level of expansions; for the same materials subjected to $T = 38^\circ\text{C}$, weight increases towards

the end of the testing period and consequent increase in expansions were also observed.

- (3) The use of combined tests such as petrography/XRD of the aggregates and accelerated laboratory expansion tests for the aggregate/cement interaction is essential for evaluating the potential reactivity of aggregates.

Dutra et al. (2017) tested two aggregates by the AMBT method, according to the Brazilian standard (ABNT NBR 15577-4, 2018). One of the aggregates tested was manufactured sand of basaltic composition from Alegrete and the other was natural sand from Ibicuí River, innocuous sand from Tietê River was used as control aggregate. A Portland cement CPV ARI with an alkali content of 0.59% $\text{Na}_2\text{O}_{\text{equi}}$ was used in the manufacture of the mortar bars. The results classified both aggregates as potentially reactive (expansion $>0.19\%$ at the end of 14 days), except for the control aggregate. SEM analyses confirmed the presence of gel in the voids of the mortar bar with the basaltic manufactured sand. The authors concluded that both aggregates were potentially reactive according to the AMBT method.

Pereira et al. (2018) studied four aggregates that are used for civil construction in the Rio Grande do Sul. Two of them are tholeiitic basalts that belong to the Paraná province in the south of Brazil (Montenegro and Campo Bom quarries); the other two are an olivine gabbro and a syenogranite (Gravataí and Porto Alegre quarries, respectively). Petrographic examination and AMBT methods in accordance with the Brazilian standards (ABNT NBR 15577-3, 2018) were used to evaluate the potential reactivity of all aggregates. For the AMBT method, a Portland cement type CP V-ARI with an alkali content of 1.0% $\text{Na}_2\text{O}_{\text{equi}}$ was used; the mortar was made with a w/c ratio of 0.47 and graded aggregates (0.30-4.75 mm). The bars were immersed in 1N NaOH solution at 80°C and measurements were taken up until 30 days; the aggregate is considered potentially reactive when the expansion is equal to or higher than 0.19% at 30 days and innocuous when it is lower than 0.19% (ABNT NBR 15577-1, 2018). The results of the petrographic examination revealed that one of the basalts contained 12-15% of volcanic glass and green celadonite filling amygdules, while no volcanic glass was found in the other basalt. The granite exhibited deformed quartz. The AMBT results showed both basalts as potentially reactive, the one incorporating volcanic glass being the most reactive (expansion of 0.46% and 0.36% at the end of 30-days); the other two rocks were considered potentially innocuous (expansion of 0.11% at the end 30-days). The authors concluded that the basalts are potentially reactive and recommended avoiding the use of volcanic rocks with vesicles filled with celadonite.

Tiecher et al. (2018) conducted a petrographic study for determining the potential reactivity of two volcanic rocks, basalt and rhyolite. The former corresponds to a fine-grained rock

composed of plagioclase, pyroxene, opaque minerals, clay minerals and mesostasis, phenocrysts of plagioclase, pyroxene, Fe and oxides and some traces of apatite and hematite. XRD analyses further identified the presence of quartz and smectite clay minerals in the rock. The (fine-grained) rhyolite was found to be composed of plagioclase, pyroxene, Ti-magnetite, quartz, K-feldspar and mesostasis and traces of apatite, hematite and clay minerals. Mesostasis consists of micro- to cryptocrystalline phases that in optical microscopy look like amorphous material but are not volcanic glass. Different types of mesostasis were identified in the same rock: (1) microcrystalline mesostasis; (2) mesostasis with better-crystalized grains; and (3) mesostasis with a predominance of clay minerals. The first has low crystallinity, is rich in silica and alkalis, and includes small grains of hematite and needles of apatite, as well as grains of quartz or feldspar that cannot be individualized. The second one includes disseminated quartz grains that can be visualized in optical microscopy, and which are associated with feldspar, clay minerals and apatites. The last one is formed by cryptocrystalline quartz-feldspar accompanied by abundant clay minerals (smectites) that form well-developed aggregates, with fibro-radiated forms, of greenish colour. The authors observed that the distribution of the mesostasis is different in the two rocks. For basalts, the mesostasis is disseminated amongst the grains; whereas for rhyolite, the mesostasis appears in higher concentrations and is distributed radially. The SEM/EDS highlighted differences between the three types of mesostasis. The mesostasis with a predominance of clay minerals shows plagioclase and pyroxenes with a flat aspect while clay minerals show scaling; the microcrystalline mesostasis is very homogeneous and consists mainly of microcrystalline quartz; the mesostasis with better-crystalized grains is homogeneous too and it contains micrograins of quartz. The AMBT results classified both aggregates as potentially reactive. The authors concluded that the interstitial material present in volcanic rocks is quite heterogeneous, which was confirmed by the presence of three types of mesostasis with the occurrence of quartz and clay minerals, some of them being visible under the optical microscope. The AMBT results led to the conclusion that the presence of mesostasis increases the expansion. The authors assumed that the composition of the mesostasis and its distribution within the rock are the main factors affecting their alkali reactivity, although they agreed that a larger number of samples should be analyzed to confirm these assumptions.

Czech Republic - volcanic rocks

About 34% of the crushed aggregates produced in the Czech Republic come from volcanic rocks; these include basalts, andesite and rhyolite, among other terms used for volcanic rocks classification (Šťastná et al., 2019).

The discovery in the 1990s of extensive concrete deterioration on highway D11, which connects Prague to Poděbrady, led to the beginning of an investigation program on ASR in the country (Lukschova, 2008; Fernandes et al., 2017). Since then, several studies have been conducted to determine the potential alkali-reactivity of different aggregates (Seidlová et al., 2012). Fernandes et al. (2017) compiled a list of aggregates in the Czech Republic that were found to be reactive either by field experience or by laboratory testing. Quarried acid volcanic rocks are considered medium to highly alkali-silica reactive according to laboratory testing.

Seidlová et al. (2012) used the AMBT (ASTM C 1260), Gel Pat Test and microscopic methods to investigate the potential reactivity of several volcanic rocks from the Bohemian Massif. These included basalts, spilites (altered basalts), diabase, melaphyres, phonolite and rhyolite. SEM/EDS revealed that only melaphyres and spilites contained fine-grained quartz, filling small voids or included in the matrix, respectively. The results of the AMBT showed low expansions for basalts (0-0.0024%), phonolites (0.002-0.011), and diabase (0.04%), while one spilite and rhyolite gave 14-day expansions of 0.282% and 0.15%, respectively. The presence of alkali-silica gel was detected in the mortar bar for the rhyolite sample and the GPT for the spilite sample. The authors concluded that: (1) a medium degree of ASR was found related to the acid volcanic rocks such as rhyolite and melaphyre; (2) the rest of the samples indicated a low degree of ASR except for one spilite sample (altered oceanic basalt) that gave high ASR potential. The authors presumed that the reactive spilite was subjected to spilitisation associated with albitization, and to the formation of chlorite, SiO₂-rich accumulations as well as quartz-rich veins. They considered that the reactivity can be due to the formation of SiO₂-rich accumulations, veins and dykes that can be deleterious due to ASR.

Šťastná et al. (2019) used the mortar bar test and petrographic techniques to evaluate the potential alkali-reactivity of seventeen volcanic aggregates from the Bohemian Massif. The samples included ultrabasic, basic, intermediate and acid rocks. Based on the AMBT test results, the authors divided the samples into four groups, from very low ASR potential to high ASR potential:

- (1) Group I – very low ASR potential (expansion <0.05%)
Ultrabasic (nephelinite-melilitite, tephrite-basanite, and picro-basalt composition) and basic (basalt and basalt-trachyandesite composition) volcanic rocks;
- (2) Group II – low-to-medium ASR potential (expansion 0.05%-0.10%)
Basic (trachybasalt) and acid (trachydacite)
- (3) Group III – medium ASR potential (expansion 0.10%-0.20%)
Basic (basalt), intermediate (andesite) and acid (rhyolite)
- (4) Group IV – medium ASR potential (expansion > 0.20%)

Acid (dacite)

The petrographic examination showed that rocks of the first group are composed of the following typical mineral assemblage: plagioclase and mafic minerals plus clay minerals (smectite), secondary carbonate (calcite) and a very rare presence of quartz. For the second and third groups, K-feldspar was often accompanied by SiO₂-rich glass and clay minerals, while cryptocrystalline to fine-grained quartz was frequently present in the groundmass together with chlorite and albite, also, calcite and dolomite occurs in veins and intergranular fillings. The fourth group showed fine-grained quartz, SiO₂-rich glass and clay minerals. The authors concluded that the rocks from Group I have almost no ASR potential, while the rocks from Group II, III and IV were considered potential reactive due to the increasing content of SiO₂-rich phases (volcanic glass, cryptocrystalline fine-grained quartz) present in the rock, as well as k-feldspar.

Iceland – Basalt and rhyolite; gravel

In Iceland, several ASR problems were reported in concrete housing because of the use of volcanic aggregates. Considerable research has been conducted to stop ASR in concrete structures, but according to Wigum et al. (2007) and Lindgård et al. (2017), little has been done in Iceland to attempt to classify the alkali-reactive components.

According to Sveinsdottir and Wigum (2003), the aggregates used in Iceland incorporate fluvial and glaciofluvial sediments, sea-dredged aggregates and crushed rocks, where the main aggregate production comes from sand and gravel sources.

Wigum et al. (2007) and Lindgård et al. (2017) affirm that basalts are the dominant rock type in Iceland and can be subdivided into alkaline and tholeiitic. The authors emphasize that the tholeiitic basalt is oversaturated in silica, which can contain cristobalite, tridymite and quartz within the glassy groundmass. Another potentially reactive rock type is rhyolite. It is formed by phenocrysts of quartz and alkali feldspar embedded in a glassy or cryptocrystalline groundmass, the reactive components corresponding to the volcanic glass and cryptocrystalline quartz. Other rocks are mentioned by Helgason (1990), like andesite (icelandite) and dacite, which are considered the most damaging in terms of ASR.

Wigum et al. (2007) and Lindgård et al. (2017) refer to a work conducted by Helgason (1982), where the author studied rock samples from the tholeiitic series through the use of the mortar bar test (ASTM C 227, 2010). The results classified the olivine basalt as innocuous but dacite, rhyolite and tholeiitic basalt (a quartz normative basalt) were considered highly reactive.

The author believed that the reactivity of this basalt was due to the presence of reactive silica minerals and interstitial glass.

Katayama et al. (1996) used petrographic examination (microscopy, XRD and EMPA) to study the potential alkali-reactivity of volcanic aggregates from western and southwestern Iceland. The results of the petrographic examination were correlated with those obtained with the mortar bar test (ASTM C 227, 2010). The samples included an olivine tholeiitic basalt, a tholeiitic basalt, basaltic andesite, dacite, Raudmelur sand and Hvalfjoudur sand. The olivine tholeiitic basalt (i.e. undersaturated basalt) revealed the presence of less than 5% of rhyolitic interstitial volcanic glass with $\text{SiO}_2 > 80\%$ according to the EMPA analysis, but no silica minerals were present. The tholeiitic basalt (oversaturated basalt) presented cristobalite and quartz in the groundmass and traces of rhyolitic interstitial glass together with smectite. The basaltic andesite contained almost 10% of rhyolitic interstitial glass with 77% of SiO_2 content and traces of cristobalite; also, some of the glass has been altered to smectite. The dacite showed some alteration with the presence of smectite; the silica is present in the form of tridymite, cristobalite and quartz and some of the glass is devitrified with a crypto-to microcrystalline texture. The Raudmelur sand presented all the range of volcanic glass from basaltic (sideromelane) to rhyolitic in composition; the sand is composed of fresh basalt (55%), sideromelane (30%), altered basalt (palagonite – 10%), plagioclase, olivine and other rock fragments. The Hvalfjoudur sand is a sea-dredged sand with altered basalt (80%), fresh basalt (10%), rhyolite, andesite, sideromelane, secondary minerals and shell fragments. The altered basalt contained vesicles often filled with smectite and sometimes lined with secondary opal or chalcedony and also zeolite and cristobalite bordered by smectite. The results obtained for the mortar bar test at the end of 52 weeks showed that only the Raudmelur sand was considered innocuous. The authors concluded that: (1) the high reactivity of the Hvalfjoudur sand is due to the presence of secondary opal and chalcedony combined with cristobalite and rhyolitic glass; (2) basaltic rocks are normally considered non-reactive when they are glassy and present fresh basaltic glass; (3) basaltic rocks with rhyolitic interstitial glass and highly crystalline may be considered potential reactive; (4) rocks oversaturated with silica commonly contain cristobalite and/or tridymite. The authors also concluded that the connection between the mineralogy and the potential reactivity of the Icelandic rocks is similar to other volcanic aggregates studied from New Zealand and Japan.

Wigum et al. (2007) used four different methods (RILEM AAR-2, ASTM C 227, RILEM AAR-3 and RILEM AAR-4) to evaluate the potential reactivity of eight different Icelandic aggregates. All of the above methods were also used to evaluate the effect on the expansion of nine different types of cement and pozzolans with one selected aggregate. The alkali content of the

(main) cement used in all tests was 1.5% $\text{Na}_2\text{O}_{\text{eq}}$. Most of the aggregate samples studied correspond to natural sand and gravel, while only two are crushed rocks/pillow lava. The samples came from different parts of Iceland: two from the Reykjavik region (A – crushed rock/pillow lava; E – natural sand and gravel), two from the West region of Iceland (B - natural sand and gravel; G - natural sand and gravel), Hvalfjörður (C - crushed rock/pillow lava), Northern Iceland (D - natural sand and gravel), Eastern Iceland (F - natural sand and gravel), southeastern Iceland (H - natural sand and gravel). Sample A is a crushed rock/pillow lava composed of unaltered basalt, well crystallized and unaltered basaltic glass. Sample B is a natural sand and gravel material formed by unaltered well-crystallized basalt, basaltic glass, altered basalt and minor amounts of very altered basalt and altered basaltic glass. Sample C is a crushed rock/pillow lava with unaltered rhyolite and traces of unaltered basalt. Sample D is a natural sand and gravel material with very fine crystalline and unaltered basalt, some dolerite particles with bigger crystals and no glass and many particles containing a glassy matrix. Sample E is a natural sand and gravel material and is composed of slightly altered or unaltered basalt, unaltered basaltic glass and shell fragments. Sample F is a natural sand and gravel material that consists of unaltered or slightly altered basalt, well crystallized with minor quantities of sediments, glass and tuff. Sample H is a natural sand and gravel aggregate with slightly crystallized rhyolite, unaltered basalt, altered basalt and basaltic glass. The laboratory tests provided different results: (1) all the samples were classified reactive for the RILEM AAR-2 method at the end of 14 days (Expansion: A= 0.29%; B=0.51%; C=0.34%; D=0.80%; E=0.29%; F=0.33%; G=0.62% and H=0.71%); for the ASTM C 227 method, only samples B, D, G and H were considered reactive at the end of 52 weeks (Expansion: B=0.32%; D=0.37%; G=0.38% and H=0.66%); for the RILEM AAR-3 method, only samples B and H were considered reactive at the end of 52 weeks (Expansion: B=0.06% and H=0.52%); for the RILEM AAR-4 method, most of the samples were considered reactive at the end of 20 weeks (Expansion: B=0.03%; C=0.05%; D=0.03%; E=0.03% and H=0.42%). Sample B was also tested with different types of cement (from 0.2-0.4% to 1.6% $\text{Na}_2\text{O}_{\text{eq}}$) and pozzolanic combinations (0 to 6% silica fume and 3% ground rhyolite); all combinations were considered reactive in the AAR-2 method, while most combinations were classified as non-reactive by the AAR-3 and AAR-4 except 1.5% $\text{Na}_2\text{O}_{\text{eq}}$ and 0% of silica fume. The macroscopic examination of the cut surface prepared for thin sections showed the presence of a white secondary product in samples A, B, E, F and H and cracks in samples D and H. In sample A, deposits of alkali gel were identified in the pores of the basaltic aggregate; some white material was observed around the aggregate particles of sample B; in sample E, small quantities of white material were observed around one aggregate particle; in sample F, a white material was exposed

around a dark aggregate particle and in sample H, some white material was exposed around aggregate particles. In sample C, zoning was detected around the particle aggregates and pop-outs associated with reactive particles near the concrete surface. Under the polarizing microscope, alkali gel was found only in samples A and H, while cracks were only found in sample H. In sample A, the gel was filling partly one air-void, while the gel was partly filling a crack in sample H. The authors assumed that no attempt was made on further petrographic classification; however, they concluded that a high reactivity occurs when large amounts of altered basalt or crystallized rhyolite compose the aggregate.

Japan – Andesite and basalt

In Japan, andesite has been one of the rocks responsible for the deterioration of different concrete structures (Katayama and Sakai, 1998; Katayama et al., 2008; Okuyama and Torii, 2008; Torii et al., 2008; Sato et al., 2009; Torii et al., 2016; Yamada and Miyagawa, 2017). According to Katayama and Kaneshige (1986), andesites are the major source of volcanic aggregates in the country and it is known that it contains an excessive amount of SiO_2 .

Yamada and Miyagawa (2017) made a list of typical rock types that may include reactive minerals; among them, there are volcanic rocks such as andesite, dacite, some basalts and tuffs. According to Katayama and Sakai (1998), the volcanic rocks that caused ASR in concrete are: (1) dark-coloured glassy andesites that contain rhyolitic glass with more than 70% of SiO_2 ; (2) light grey coloured, holocrystalline andesites and dacites with no glass but with cristobalite or tridymite; (3) devitrified rhyolite containing cryptocrystalline quartz.

Several works on the potential reactivity of volcanic aggregates have been published by Katayama (Katayama and Kaneshige, 1986; Katayama et al., 1989, Katayama, 2010), Wakizaka (Wakizaka, 2000) and Yamada (Yamada et al., 2014, Yamada and Miyagawa, 2017).

Katayama and Kaneshige (1986) studied the diagenetic changes in potential alkali-reactive volcanic rocks in Japan. In this study, different alteration zones are attributed by the authors to the Japanese volcanic rocks: (1) unaltered zone with rocks of Quaternary age and Pliocene to Pleistocene volcanoes; (2) slightly altered zone limited mainly to Pliocene to Pleistocene volcanoes and Pliocene volcanic rocks; (3) smectite zone with volcanic rocks from middle to late Miocene, and (4) chlorite zone from early Miocene to Cretaceous age. These different zones were observed and characterized from the point of view of petrography.

- The unaltered zone contains fresh volcanic rocks where volcanic glass is preserved and no secondary minerals are present: basalts frequently show well crystallized intergranular

texture but some have small amounts of dark brown volcanic glass in the groundmass and also the presence of cristobalite; andesites have intersertal texture that may contain pale brown to colourless glass, cristobalite and tridymite, the latter being exclusive of these rocks.

- In the slightly altered zone, devitrification of volcanic glass starts and recrystallization of the groundmass starts to occur; the groundmass tends to be coarse with secondary intergrowths of minerals such as spherulites (normally radiating fibers of feldspar and interstitial tridymite or cristobalite), in a cryptocrystalline groundmass. The rhyolitic glass presents perlitic cracks.
- The smectite zone include volcanic glasses and mafic minerals replaced by clay minerals such as smectite, either in basalts or in andesites; in the case of dacites and rhyolites, volcanic glass is recrystallized into quartz and feldspar with some disseminating smectite. Cristobalite and tridymite present in the original rocks are usually preserved; in some altered andesites, cristobalite is visibly lined by greenish-brown smectite pseudomorphs after an intersertal texture; opal and zeolites may also appear by replacing the volcanic glass and other minerals or in vesicles and cracks in the rock. When the degree of alteration is higher, smectite alters into chlorite.
- In the chlorite zone, basalts and andesites rich in mafic minerals change to greenish rocks with a predominance of chlorite. Vesicular basalt tends to have an amygdaloidal texture and andesites alter to greenish propylite with a granular texture. Regarding cristobalite and tridymite, they altered to coarse aggregates of stable quartz. In the felsic rocks (e.g. rhyolite), the glassy to microcrystalline groundmass alters to stable quartz and feldspar. albitization and sericitization also occur in this zone.

The authors emphasize that the andesites that belong to the first two zones (unaltered and slighted altered zones) are the ones that are causing the deterioration of concrete in the country. In addition, the pop-outs in concrete have been attributed to reactive opal from the smectite zone. The authors used a quick chemical test that has already been withdrawn; in the results of this test, younger volcanic rocks were considered potentially reactive to reactive due to the presence of reactive minerals, while older rocks were classified as innocuous due to the scarcity of reactive components. In the end, the authors concluded that the potential alkali reactivity of volcanic rocks gradually decreases from the unaltered zone to the chlorite zone.

A study performed by Katayama et al. (1989) compared volcanic rocks from Japan and New Zealand by using chemical analysis, XRD, EMPA, norm calculations and ASTM 289 chemical method. The phosphoric acid method and the SEM/EDS were only done for the Japanese rock samples. Silica minerals (cristobalite and tridymite) and interstitial volcanic

glass were found to be widespread in rocks like andesites and basalts in Japan. The results highlight a similarity of volcanic rocks in both countries because they contain the same ranges of interstitial volcanic glass, cristobalite and tridymite. Focusing on volcanic rocks from Japan, the authors collected forty-two rock samples that included mainly andesites, but also basalts, dacites and rhyolites. The majority of the Japanese basalts are oversaturated with silica, as well as the andesites, dacites and rhyolites. Optical microscopy revealed that cristobalite appears in basalts and andesites as fine mosaic aggregates in the groundmass or rounded patches; tridymite occurs as coarse mosaics filling the interstices of the groundmass in andesites; volcanic glass is present either in the groundmass or sometimes enclosed in phenocrysts and is usually dark brown in basalts and pale brown in andesites; quartz is present as rounded patches of sponge-like aggregates in a poorly crystallized groundmass. The phosphoric acid method detected cristobalite, tridymite and also quartz in the samples. The authors sustain that the amount detected by this method exceeds significantly what was observed by optical microscopy. The EMPA analysis of volcanic glass from the different rock samples showed that they contained rhyolitic glass in the range of 72-78% silica, even in basalts. The authors affirm that rhyolitic glass is present in different rocks whether they are basalts, andesites, basalts, dacites or rhyolites. The correlation of the results with the reactivity led the authors to conclude that:

- (1) to show potential reactivity, a fresh volcanic rock must contain more than 50% of silica and must be saturated or oversaturated with silica for siliceous volcanic glass, tridymite and cristobalite;
- (2) the potential reactivity of rocks with a matrix completely glassy depends solely on the amount of glass, normally with more than 65% of silica and in general falls in the range of 72-78% silica;
- (3) the reactivity of rocks where glass is completely absent depends on the amount of silica minerals present;
- (4) the reactivity of altered rocks where devitrified glass is present is not known but the excess of silica given by the CIPW norms calculation suggests the presence of cristobalite, tridymite or quartz. Most normative quartz is present as cristobalite or tridymite.

The authors also highlight that to make a good assessment of the potential reactivity of volcanic rocks, a petrographer should combine different test methods and analyses of the rocks, including bulk chemical composition, optical microscopy, phosphoric acid and XRD analysis.

In 1997, Katayama (1997a, 1997b) published two articles, one of them making a review of alkali-silica reaction in Asia (Katayama, 1997a), while the other deals with the petrography for alkali-silica reactivity in concrete (Katayama, 1997b). In both articles, the author discusses the pessimum phenomenon that depends on the reactivity of minerals. According to the author, the pessimum proportion increases with the decrease of the reactivity: opal (< 5%), cristobalite (< 10%), tridymite (< 10%), chalcedony (20%), cryptocrystalline quartz (50%), microcrystalline quartz (> 80%), rhyolitic glass (100%), dacitic glass (100%). Regarding the basaltic and andesitic glass, only the result of the chemical test is referred to, which gave the andesitic glass at the boundary of innocuous/deleterious and basaltic glass as innocuous. Katayama (1997b) divided the rocks into early, moderate and late expansive rocks. The early expansive rocks included, among others, andesite and dacite; the moderate variety comprised devitrified rhyolite, flint and chert and the late expansive ones contained sedimentary (impure limestone), igneous (granite and devitrified rhyolite) and metamorphic rocks (metaquartzite). The author also discussed the oversaturation of silica in different volcanic rocks, which represents the excess of silica (normative Q) that could be present as cristobalite, tridymite and quartz in: slowly cooled well-crystallized basalt (Q < 5%), andesite (Q 5-20%), dacite (Q 20-35%) and rhyolite (Q > 35%). For rapidly cooled rocks, the excess silica enters the volcanic glass, volcanic glass with silica content higher than 65% is considered reactive. Opal, cristobalite, tridymite and chalcedony are highly reactive and present a marked pessimum phenomenon in the mortar bar test. On the contrary, volcanic glass does not show a pessimum phenomenon. According to the author, light-coloured well-crystallized volcanic rocks with cristobalite and tridymite tend to have small pessimum proportions (< 20%); dark-coloured glassy rocks do not have it (100%); partly crystallized rock with rhyolitic volcanic glass and silica minerals present intermediate pessimum proportions. In rocks like rhyolite, the presence of silica minerals occurs in young well crystallized rocks while secondary quartz occurs in older rhyolites. For moderate to late expansive rock, devitrified rhyolite contains less reactive crypto and microcrystalline quartz derived from rhyolitic glass.

Wakizaka (2000) studied the reactivity of Japanese rocks from rock samples obtained either from coarse aggregate in concrete structures or from quarries. Part of the study included igneous (volcanic: andesites, basalts, dacites and rhyolites, among others), sedimentary and some metamorphic rocks collected from different quarries and outcrops and that were subjected to the chemical and mortar bar tests. The results showed that the volcanic rocks showing reactivity in both methods were basalt, andesite, dacite and rhyolite. For the author, most volcanic rocks with large dissolved silica concentrations have reactive minerals and the solubility of cristobalite, tridymite and volcanic glass is very high in the presence of an alkaline

solution. Another issue that is discussed by the author is the devitrification of volcanic glass; the devitrification occurs with time and in some devitrified parts of the rock, cristobalite and tridymite are present; however, the percentage of reactive minerals becomes low when chlorite is present in the rocks. The author assumed that chlorite percentage increases with age and that the presence of reactive minerals is inversely related to the degree of alteration. The author concluded that the reactivity of volcanic rocks is due to the presence of cristobalite, tridymite and volcanic glass in the rock, which is indirectly controlled by the age and alteration of the rock.

Kawabata et al. (2007) used the petrographic method to investigate the alkali-silica reactivity of andesite in various alkali supplying conditions. Eighteen aggregates were studied, where the majority of the samples included andesites with different degrees of alteration ($An_{(A)}$, $An_{(C)}$, $An_{(F)}$, $An_{(I)}$, $An_{(J)}$, $An_{(L)}$, $An_{(M)}$, $An_{(N)}$, $An_{(O)}$, $An_{(P)}$, $An_{(Q)}$, $An_{(R)}$); other rocks in this study included dacites, one basalt and one rhyolite. Two samples of andesite contained only glass and no silica minerals were present ($An_{(M)}$, $An_{(N)}$). The contrary occurs in two other andesites where no volcanic glass was present, only silica minerals ($An_{(Q)}$, $An_{(R)}$). The rest of the andesites contain silica minerals such as quartz, cristobalite and tridymite with only one or two being present at the same time. For the basalt sample, silica minerals were present, only volcanic glass. The chemical test method showed that three of the samples were considered innocuous, one of them being a basalt and the other one andesite ($An_{(P)}$). According to the authors, this andesite is severely altered and reactive silica minerals are assumed to be altered into less reactive quartz; also, the geochemical analysis showed an LOI of 4.40%wt for the same sample. The results of the AMBT method showed that the samples containing reactive silica minerals gave large expansions; the two andesites that included no silica minerals but volcanic glass showed no expansion in this test. The authors state that volcanic glass is judged “non-reactive” in saturated NaCl solution, being its dissolution is extremely low. According to the authors, its solubility depends on the pH of the pore solution. On the other hand, cristobalite shows high solubility in saturated NaCl solution. The authors believe that the reactivity of andesite depends on its dissolution behaviour and pore solution composition. The results showed the glassy andesite as innocuous, even in specific environments such as deicing salt and seawater.

Yamada et al. (2014) used eighteen concrete mixtures to examine the effect of the type and content of aggregates. Andesites, hornfels and limestones were used as aggregates. One of the andesites (A - coarse, B - fine) contained opal veins, cristobalite and volcanic glass; the other andesite (C) contained tridymite but no volcanic glass. The chemical method (ASTM C 289) classified the first andesite (A, B) as potentially deleterious and the other as deleterious,

the rest of the rock samples being considered innocuous. The CPT method was applied to the eighteen mixtures according to a similar version of RILEM AAR-4, MJASS5Nm where the prisms were wrapped with wet paper. The RILEM AAR-4 method was only performed for five mixtures and the results were compared with the mixtures from MJASS5Nm. For the CPT method, according to MJASS5Nm, different admixtures of fly ash (nine mixtures) and ground granulated blast furnace slag (one mixture) were used. The CPT results obtained at the end of 26 weeks showed:

- (1) an expansion of 0.21% for the first andesite (A/30% mixed by mass ratio) without any admixture;
- (2) the highest expansion (expansion: 0.51%) was obtained when fine andesite (B/30% mixed by mass ratio) was used with no admixtures and together with a coarse limestone;
- (3) an expansion of 0.30% for the other andesite (C/30% mixed by mass ratio).

The pozzolanic materials were more effective in some mixtures than in others, with the expansion being completely suppressed in some cases, while only slowed down in other cases. The comparison between the MJASS5Nm and RILEM AAR-4 showed that the latter gave less expansion.

Turkey – basalt and rhyolite

Several studies have been conducted regarding the potential alkali-reactivity of different volcanic aggregates from Turkey. Some of these studies (Korkanc and Tuğrul 2004, 2005; Çopuroğlu et al., 2009; Tapan, 2015; Rızaoğlu, 2017) incorporated different types of volcanic rocks that range from basalts to rhyolites.

Korkanc and Tuğrul (2004, 2005) studied eleven basalts from the Middle Anatolian Region of Turkey, those being considered the major source of locally crushed rock aggregates. Petrographic techniques and an accelerated mortar bar test were used to evaluate the potential alkali reactivity of these aggregates (Korkanc and Tuğrul, 2005) and also physicommechanical properties of the aggregates were determined (Korkanc and Tuğrul, 2004). The eleven aggregates were classified according to their macroscopic characteristics, such as colour, texture, pores, and fractures: basalts (MV1, MV2, MV5 and MV6), olivine basalts (MV3, MV4, KV1, KV2, KV4 and 1B1) and basaltic andesite (KV3). However, the geochemical analysis categorized them into different groups: basalts (IB1, KV1 and KV2), basaltic andesites (KV4, MV3 and MV5), andesite (KV3) and dacites (MV1, MV2, MV4 and MV6). Korkanc and Tuğrul (2004, 2005) maintained the first classification of the rocks based on the macroscopic characteristics instead of the one obtained through the geochemical analysis for the entire study. The petrographic examination showed that the KV3 sample contained in its matrix

mainly unweathered volcanic glass (43.6%) and the sample IB1 matrix is formed by abundant plagioclase microcrystals and a lesser amount of volcanic glass. It also contains epidote, calcite, and chlorite as secondary minerals. Samples MV5 and MV6 contain a higher percentage of secondary epidote (approximately 4.5%) as a hydrothermal alteration product. The MV3 and MV4 samples also contain epidote as a hydrothermal alteration product (3.5%). The samples MV1, MV2 and MV5 have a composition between basalt and andesite. They are composed of clinopyroxene (augite) with a lesser amount of opaque minerals, in a matrix formed by plagioclase microcrystals. The authors state that no quartz polymorphs were observed in the studied basalts. The results of the accelerated mortar bar test after 14 days of testing show that the MV5 sample has the highest expansion (0.163%) and KV1 has the lowest expansion (0.009%). The MV1, MV5, MV6, and KV3 showed expansions above 0.10%. The mortar bars were also examined by SEM, which confirmed that the samples from MV1, MV5, MV6, and KV3 show the occurrence of alkali-silica gel (Korkanc and Tuğrul, 2005), with visible expansion cracks in alkali-silica gel in the MV6 and KV3 samples (Korkanc and Tuğrul, 2004). The mechanical (e.g. Aggregate impact and crushing value) and physical (e.g. aggregate shape, relative density, bulk density and water absorption) properties show that olivine basalts have better performance when compared to the basaltic andesite (Korkanc and Tuğrul, 2004). Korkanc and Tuğrul (2005) affirm that the reactivity of the samples studied is controlled by the presence of volcanic glass, alteration minerals and by more than 50% of SiO₂ content. The authors also concluded that the basalts having the acidic-intermediate character or volcanic glass in their matrix show expansion generally higher than 0.10% at the completion of the test, and they are considered potentially alkali–aggregate reactive. The rest of the samples show little expansion, which led the authors to assume that this might be related to the fact that basalt aggregates are insufficiently reactive, the amount of reaction products is not enough to cause expansion or is not sufficiently expansive.

Çopuroğlu et al (2009) reported an alkali-silica reaction performance of basalt from Western Anatolia. The authors state that the rock caused severe gel formation in the concrete microbar test. Their study included petrographic examination, geochemical analysis and expansion testing. Optical microscopy confirmed the occurrence of brown glass in many phenocrysts and the presence of dark brown isotropic glass groundmass. From the point of view of petrography, the authors classified the rock as a clinopyroxene-olivine basalt but the geochemical analysis classified the rock as andesite. The AMBT method (RILEM AAR-2) classified the rock as reactive with an average 14-day expansion of 0.556%. An EDS analysis was made on the matrix glass that revealed variations in the Na₂O, CaO, MgO, F₂O₃ and TiO₂ content while K₂O, Al₂O₃ and SiO₂ contents are relatively constant. The SiO₂ content of the glass gave an average

of 67.5% wt. The authors concluded that a basalt containing 70% of silica in the glass could be alkali-reactive and deleterious to concrete structures. The authors also concluded that the dissolution of glass in the matrix of the basalt can cause: (1) formation of ASR gel; (2) increased porosity and permeability of the basalt matrix; (3) reduction of mechanical properties of the aggregate and (4) additional gel formation within the aggregate.

Tapan (2015) studied nine different alkali volcanic samples from the Lake Van region (Etrüsk volcano, Girekol volcano, Timar, Yüksektepe and Bendimahi) to determine their alkali-silica reactivity. The author used mainly petrographical analysis, geochemical analysis and the AMBT method. The rocks studied included one tephrite (BEND), two basalts (TIMAR and YB), two hawaiits (AH and GH), two trachytes (HT and ET), one trachyandesite (ETRA) and one rhyolite (ER). From the petrographic point of view, the basic rocks (BEND, TIMAR and YB, AH and GH) present crystalline groundmass and volcanic glass and the intermediate to acid rocks (HT, ET, ETRA and ER) show volcanic glass with crystalline and glassy groundmass. Clay minerals are present in the intermediate and acid rocks except for one of the trachytes (HT). The geochemical analysis showed that five of the nine samples have more than 50% of SiO_2 . Regarding the AMBT (ASTM C 1260), the results showed that the rocks with higher silica content (HT, ET, ETRA and ER) were considered deleterious, with 14-day expansions ranging from 0.24% to 0.42. The SEM analyses conducted on the mortar bars revealed cracks and the occurrence of alkali-silica gel in the samples considered deleterious by the AMBT method. The author determined that there is a correlation between the geochemical test and the AMBT method, the samples with $\text{SiO}_2 > 50\%$, $\text{K}_2\text{O} < 3\%$, $\text{CaO} < 5\%$ and $\text{MgO} < 3\%$ are considered deleterious. The same author recognizes that the SiO_2 content of aggregates by itself is not enough to classify an aggregate as innocuous or deleterious from the point of view of ASR.

Rızaoğlu (2017) studied the Göksun ophiolite in Kahramanmaraş to determine the alkali reactivity of the rocks existent in the ophiolite. Basalt, basaltic-andesite, andesite, dacite and rhyolite are some of the different compositions present in the rock units. The author used different methods to evaluate the alkali reactivity of the samples, such as petrographic examination, geochemical analysis and AMBT method. The samples included two basalts, four basaltic andesites, two andesites, four rhyolites and one dacite. The petrographic examination showed that most of the basic and intermediate samples contained calcite, chlorite and epidote as the filler material of the pore spaces and as secondary alteration products. Phenocrysts of quartz and plagioclase are dispersed in a groundmass composed of K-feldspar and plagioclase microcrystals in rhyolite. In dacite, there are phenocrysts of plagioclase and quartz and secondary alteration minerals like epidote, chlorite and rare calcite. Most of them contain glass in the groundmass displaying intersertal textures. The results of ASR tests showed that

the basic (basalt) and acid rocks (rhyolite and dacite) are considered innocuous, with an expansion ranging from 0.01% to 0.09%. For the intermediate rocks (Basaltic andesite and andesite), some are within the boundary, and others within the potentially reactive area; the expansions range from 0.10% to 0.29% for basaltic andesite samples and from 0.05% to 0.17% for andesite. The results obtained by the different methods lead the author to conclude that intermediate rocks are more prone to be ASR reactive than basic and acidic rocks. Also, it was estimated that the glassy matrix of the intermediate rocks is partly responsible for the alkali-silica reactivity

United States of America (Hawaiian Islands) - Basalt

A study completed by Robertson and Shen (2018) compared laboratory testing with a field evaluation of concrete, both made mainly with local aggregates. This field exposure site project started due to a report in 2003, of deteriorated concrete at Tripler Army Medical centre in Oahu. After that, a test program was initiated by the University of Texas and the University of New Brunswick, Canada, funded by the Federal Highway Administration (FHWA), where a field site was created on Oahu to evaluate the potential for ASR by using local Hawaiian aggregates. This exposure site is located at the Magoon Research and Instruction Facilities, being part of the University of Hawaii at Manoa. Blocks, 0.38 x 0.38 x 0.71 m, in size, were made from 40 concrete mixes that incorporated aggregates from Hawaiian aggregate sources, and some US mainland aggregates (Placitas from New Mexico, Jobe and Wright from Texas) known to have ASR expansion (Thomas et al., 2013a).

Laboratory testing (AMBT 80°C - ASTM C 1260 and CPT 38°C - ASTM C 1293) was also conducted on local aggregates, either coarse (Kapaa/Ameron, Oahu; Halawa, Oahu; Hilo, Hawaii and Waimea, Hawaii) or fine (Kapaa/Ameron, Oahu; Halawa, Oahu; Hilo, Hawaii and Waimea, Hawaii; Waikoloa, Hawaii; Maui Dune Sand and Halfway Bridge) and on a siliceous sand (Orca) from British Columbia, Canada (Thomas et al., 2013a; Robertson and Shen, 2018). The tests were performed at the University of Texas (UT) and the University of Hawaii (UH) at Manoa. The results showed that two coarse aggregates (Halawa: UT=0.627%, UH=0.130%; Hilo: UT=0.633%) and four fine aggregates (Halawa: UT=0.526%, UH=0.260%; Hilo: UT=0.718%; Waikoloa: UT=0.522%, UH=0.253%; Orca: UT=0.222% and UH=0.090%) were considered potentially reactive by the AMBT method at the end of 14 days. Regarding the CPT at 38 ° C, only the fine aggregate Waikoloa was considered reactive with expansions of 0.287% obtained by UT and 0.038% achieved by UH (Robertson and Shen, 2018). The laboratory testing was also performed on Placitas, Jobe and Wright which confirmed that all are reactive in both test methods (Thomas et al., 2013a; Robertson and Shen, 2018).

The concrete mixes used in the manufacture of the blocks involved: (1) a w/c of 0.42, a coarse-to-fine aggregate ratio of 60/40; (2) a cement with an alkali content of 1.20% $\text{Na}_2\text{O}_{\text{eq}}$ in most specimens and a low-alkali cement (0.55% $\text{Na}_2\text{O}_{\text{eq}}$) in selected specimens; (3) two different admixtures (lithium nitrate and fly ash) in some mixes. After 1.5 years, only one block presented cracking (at the end of 805 days), which was the case of Waikoloa aggregate; however, Thomas et al. (2013a) did not believe that the cracking is due to ASR because expansion is still less than 0.02% at this age. Because of the results obtained from the exposure site and the laboratory tests, 10 additional blocks were cast in 2013 with Waikoloa aggregate to confirm or not its reactivity and also to evaluate the efficacy of preventive measures. Robertson and Shen (2018) report that after four and a half years of testing, none of the new blocks showed signs of expansion, not even the block fabricated identically to the original. The same authors indicate that the initial block with the Waikoloa aggregate has continued to expand and is on an upward trend. Thomas et al. (2013a) considered doing a sampling of the block with expansion to conduct a petrographic evaluation to see if there is any evidence of ASR.

Thomas et al. (2013a) and Robertson and Shen (2018) concluded that none of the blocks with local aggregates showed signs of ASR at the end of two and six years of testing, respectively. The only exception was the first block cast with Waikoloa aggregate, and even though the second block cast with that aggregate did not reveal any signs of ASR, Robertson and Shen (2018) recommended not to use this aggregate in the future without some mitigating measures. The authors affirm that the aggregate is not currently used for concrete manufacturing. Thomas et al. (2013a) emphasize that monitoring needs to continue for at least ten years to have more data.

3.1. Petrography of volcanic rocks and ASR

Petrography is the science that describes and classifies rocks by observing the mineral properties and their fabric through the use of a polarising microscope. According to Mackenzie et al. (1982), petrography is the descriptive and factual side of petrology. Best (2003) defines petrology as the study of rocks and the conditions in which they form, seeking to understand their nature and origin. On the other hand, geochemistry deals fundamentally with the processes and consequences of the distribution of chemical elements in minerals and rocks in different physical-chemical environments (Misra, 2012). Through geochemistry, it is possible to infer the conditions that governed minerals and rock formation and evolution. For example, the use of geochemistry helped distinguish between different basalt types otherwise

impossible to separate from optical studies (Francis, 1993), and therefore the role of geochemistry is thus essential for petrology.

By definition, volcanic rock is an igneous rock that results from the eruption of magma either ejected explosively (e.g. pumice or scoria) or extruded as lava (e.g. basalt, rhyolite, trachyte). The rocks range in composition from basic (basalt) to acid (rhyolite). They are usually fine-grained, and their mineral composition and texture distinguish them from other rocks.

From the point of view of ASR, volcanic rock types such as andesite, basalt and rhyolite have been considered potentially reactive (Sims and Nixon, 2003b; RILEM AAR 1.1, 2016), and their reactivity is associated with some of their components (e.g. volcanic glass, tridymite, cristobalite). Extensively altered and devitrified volcanic rocks are often considered non-reactive according to Poole and Sims (2016). Not all of the andesites or basalts or rhyolites are considered reactive; Fernandes et al. (2015) affirm that the difference between innocuous and potentially reactive rocks depends on the type of silica present and its geological formation.

There is a range of petrographic variations in rocks from different settings that shows changes in the mineralogy with increasing SiO₂ content in the magma. Even between basalt types (e.g. tholeiitic and alkali basalts), there are some differences in petrographic and mineralogical characteristics that are described by some authors such as Wilson (1989), Winter (2001), Greenough et al. (2005).

3.2.1. Petrography of volcanic rocks at different tectonic settings

Magmatism and therefore volcanism can occur at (Wilson, 1989; Frost and Frost, 2019): (1) divergent tectonic plate margins (e.g. Mid-ocean ridge – MOR, back-arc basins); (2) convergent plate margins (e.g. Island arcs) and (3) within plates or intraplate (e.g. flood basalts provinces, intercontinental rifts, oceanic islands). Basalt, andesite, trachyte and rhyolite are examples of different volcanic rocks that occur in different tectonic settings.

Basalts are extruded along the mid-ocean ridge where a new oceanic crust is formed. According to Frost and Frost (2019), the basalts that erupted correspond to olivine and quartz-normative tholeiite and are known as mid-ocean ridge basalts (MORB). Le Maitre et al. (2002) define MORB as a tholeiitic basalt erupted at mid-ocean ridges containing Mg-olivine, Ca-rich clinopyroxene, plagioclase, titanomagnetite and variable amounts of pale brown glass. MORB is subdivided into two types: (1) N-MORB or normal MORB characterized by depletions in highly incompatible elements relative to more compatible elements and (2) E-MORB or enriched MORB in incompatible trace elements (Arevalo and McDonough, 2010).

Continental rift zones are areas with lithospheric extension characterized by a central depression, uplifted flanks and thinning of the underlying crust (Wilson, 1989). According to LaFemina (2015), at the beginning of rifting, lithospheric extension and thinning are represented topographically by normal faulting and by the formation of horst and graben structures. The lavas that erupted during the initial stages of rifting are characteristically tholeiitic basalts, but there is variability in the chemistry and petrology of the initial magma related to the mantle source. The different stages of rifting will lead eventually to seafloor spreading and the formation of oceanic crust and lithosphere. However, not all of the continental rifts reach the final stage of the process and some of them fail to evolve; the Paleozoic Oslo Graben of southern Norway is one of those examples (Wilson, 1989). On the other hand, the East African rift that extends from Syria in the north to Mozambique in the south is one of the best examples of active rifting (Corti, 2012; LaFemina, 2015).

Oceanic Islands usually occur far from divergent or convergent plate boundaries in the ocean basins (Wilson, 1989); however, some occur near oceanic ridge spreading centres like Ascension Island located in the Atlantic Ocean (Condie, 2005) and Galapagos Islands in the Eastern Pacific Ocean (Frost and Frost, 2019; LaFemina, 2015). According to Wilson (1989), in slow-spreading ocean basins, volcanic islands tend to occur singly or in small groups like in the Atlantic, while in fast-spreading oceans the islands commonly occur in linear chains like in the Pacific (Hawaiian Islands). The compositions of basalts in these islands are generally known as ocean island basalt (OIB) (Rogers, 2015) and they include both tholeiitic and alkali basalts (Frost and Frost, 2019). According to LaFemina (2015), islands like Hawaii, Tahiti, Galapagos, Reunion, the Azores, and the Canary Islands are considered oceanic islands.

Large Igneous Provinces (LIPs) are huge volumes of predominantly mafic extrusive and intrusive rock (Self et al., 2015) with outcrop areas $\geq 100\,000\text{ km}^2$, volumes of $>100,000\text{ km}^3$ and maximum life spans of about 50 my (Bryan and Ernst, 2008). The LIPs occur both on continents and in the oceans, in intraplate and on plate boundaries (Sigurdsson, 1999). Some examples of LIPs are the Etendeka-Paraná provinces in Africa and South America, which is a Continental flood basalt (CFB). Bryan and Ernst (2007) proposed another classification for the LIPs where they subdivide the LIPs into Mafic LIP and Silicic LIP. The former separates continental from ocean crustal settings while the latter is exclusively continental. The authors also state that Mafic and Silicic LIPs are compositionally bimodal, and may contain a range of compositions from basalt to rhyolite. Bryan et al. (2002) concluded that the Silicic LIPs have $\leq 10\%$ by volume of mafic igneous rocks, while mafic LIPs, of the continental flood basalt provinces, have $\leq 10\%$ by volume of silicic igneous rock. It is interesting to know that plagioclase is the dominant phenocryst either in CFB and in MORB settings, although some

distinctive differences are known between the two settings: in CFB, augite and sometimes pigeonite are the main ferromagnesian minerals while olivine and Mg-Cr spinel are very common for MORB (Frost and Frost, 2019).

Back-arc basin is the area lying behind an island arc (Wilson, 1989; Ronde and Stucker, 2015). According to Condie (2005), back-arc basins are sections of oceanic crust between island arcs or between island arcs and continents, of which the Philippine Sea and the Seas of Japan and Okhotsk, respectively, are examples. The same author affirms that this type of tectonic setting is common in the western Pacific and is characterized by a horst-graben topography.

Island Arcs occur above active subduction zones where one plate is subducted beneath the other (Condie, 2005). Volcanic arcs can form either in the oceanic or continental lithosphere (Rogers, 2015). This means that one oceanic lithosphere can subduct beneath another oceanic lithosphere, which is the case for the Izu-Bonin-Mariana Island Arc (Condie, 2005; Rogers, 2015); oceanic lithosphere can subduct beneath continental lithosphere which is the case of the Andean volcanic arc (Condie, 2005; Rogers, 2015), Cascades and Japan (Condie, 2005). The name Island Arc Basalt (IAB) is used to distinguish them from MORB due to their high content in H_2O , K_2O and Al_2O_3 (Rogers, 2015). Magmas of oceanic island arcs are dominantly basaltic (tholeiites and high alumina basalts) although highly evolved (rhyolitic) and alkaline magmas also occur (Schimnke, 2004).

Foulger (2010) states that the terms MORB and OIB are geographical designations that do not take into account that the same rocks can be found in other settings, for example: (1) MORB is also found on continents (Greenland) and oceanic Islands (Iceland); (2) OIB is found in mid-ocean ridges known as E-MORB, oceanic plateaus and on CFB and (3) less siliceous OIB – alkali basalts – are found either in oceans or continents.

In general terms, basaltic magmatism occurs in MOR, back-arc basins, LIPs, continental rifts, intraplate hotspots and subduction zones while intermediate and silicic magmatism (volcanic rocks: andesite, dacite, rhyolite; plutonic rocks: diorite, granite) is more restricted to continental crust and most common above subduction zones (Asimow, 2005).

Table 3.9 summarizes the petrographic characteristics of the volcanic rocks for each setting.

Table 3.9. Petrographic characteristics of the volcanic rocks for each setting (Wilson, 1989; Winter, 2001; Frost and Frost, 2019)

Settings	Rocks	Texture	Phenocrysts	Characteristics	Magma Series
MORB	Basalt is olivine and quartz-normative tholeiite	Glassy to highly porphyritic	Ol $\pm$ Mg – Cr spinel Pl + Ol $\pm$ Mg – Cr spinel Pl + Ol + Au	- Olivine: usually euhedral, typically with more forsterite - Spinel: Mg and Cr rich, and is frequently found as inclusions in olivine. - Plagioclase: commonly more Ca-rich in basalts from MAR than from EPR. - Clinopyroxene colourless to pale green - Groundmass: dominated by plagioclase and clinopyroxene microlites and Fe-Ti oxide phases	Tholeiite
Continental rift zone	Ranging in composition from basalt to rhyolite	From aphyric to strongly porphyritic	<u>Basanite-phonolite:</u> Basanite: Cr-spinel, Fe-Ti Oxides, cpx (agt), ol, pl.		Tholeiite and Alkaline
			Phonolite: Fe-Ti oxides, cpx (agt), amph, bt, alkali FSP, nepheline, apatite, sodalite, ol.	- In olivine, the forsterite is higher in the more basic rocks while fayalite is higher in the more acid rocks.	
			<u>Alkali basalt-trachyte:</u> Alkali basalt: Ol, pl, opaques Trachyte: opaques, cpx (agt), ol, sanidine (qz in the groundmass).	- Ca-Clinopyroxene is pale brown (aug) in the basic rocks, pale green (hd) in trachytes and rhyolites and green-yellow (agt) in phonolites. - Fe-Ti oxides are not present in the transitional basalt-rhyolite suite. - Pl ranges from bytownite-labradorite in the basic rocks to oligoclase in the acid rocks. - Apatite occurs both as phenocrysts and groundmass	
			<u>Transitional basalt-rhyolite</u> Transitional basalt: Ol, pl, cpx (agt). Rhyolite: qz, anorthoclase, cpx (hd), pl, ol, opaques		
Island Arc Volcanic Rocks*	Ranging in composition from basalt (IAB) to andesite but it can	Highly porphyritic, being tholeiitic series less porphyritic	<u>Tholeiite:</u> <u>Basalt</u> Pl, Cpx, Ol, mt, amph, opx	- In general, all the major ferromagnesian minerals are Mg rich. - Augite is the most common pyroxene in the groundmass.	Tholeiite, calc-alkaline and alkaline

Settings	Rocks	Texture	Phenocrysts	Characteristics	Magma Series
	also reach dacite and rhyolite.		<i>Andesite</i> Pl, Cpx, opx, Ol, qz, mt, amph	- Amphibole is strongly pleochroic (from green to brown in colour) and with intense opaque reaction rims.	
			<u><i>Calc-alkaline:</i></u> <i>Basalt</i> Ol, Pl, Cpx, mt, amph, opx	- Plagioclase is commonly highly calcic. - Titanomagnetite is the normal Fe-Ti oxide present. - Ilmenite is normally absent	
			<i>Andesite</i> Pl, Cpx, opx, amph, mt, ol, bi, qz	- Pigeonite is present in the groundmass of tholeiitic rocks and hypersthene is present in the groundmass of calc-alkaline rocks.	
Back-arc basin	Basalt	Basalts sparsely porphyritic		<i>Basalts</i> - The phenocrysts are sometimes set in a glassy groundmass. - Mineralogically appears similar to MORB	Tholeiite
			<i>Basalt</i> Ol + pl	<i>Andesites</i> - The andesites called boninites are glassy olivine, orthopyroxene and clinopyroxene phyric lavas	
			<i>Microphenocrysts:</i> Pl + ol + Ca rich cpx, + chr + titanomagnetite	- Absence of feldspar in all but most evolved varieties - More primitive end-members: olivine and clinoenstatite - Differentiated samples: lack olivine but may contain hornblende and Ca-plagioclase phenocrysts	
Ocean Island Volcanic Rocks	Ranging in composition from basalt to rhyolite.	<i>Porphyritic Tholeiitic Basalts:</i> intergranular	<i>Tholeiitic Basalts</i> Ol + Pl + Cpx + Opx	<i>Tholeiitic Basalts</i> - Olivine occurs only as phenocrysts - 3 pyroxenes can occur: augite (pale brown), hypersthene and pigeonite - Interstitial glass is common.	Tholeiite and alkaline
		<i>Alkali Basalts:</i> From intergranular to ophitic	<i>Alkali Basalts</i> Ol + Cpx + Pl	- No interstitial alkali feldspar and analcite - No amphibole or other hydrous phase	
				<i>Alkali Basalts</i>	

Settings	Rocks	Texture	Phenocrysts	Characteristics	Magma Series
Large Igneous Provinces (LIP) (CFB)	Ranging in composition from basalt to rhyolite.	Porphyritic, aphyric to sub-aphyric	Typical assemblage Pl + Cpx (au + pi) + Ti-mt + rare ol	- Olivine occurs both as phenocrysts and in the groundmass. - augite is titaniferous with purplish brown rims and orthopyroxene is absent. - Interstitial glass is rare or absent. - Interstitial alkali feldspar and feldspathoids may occur.	
				<i>Basalts and basaltic andesite</i>	
				- groundmass: pl + au + pi + Ti-mt + il + some glass	
				<i>Andesites and dacites</i>	
				- Phenocrysts of plagioclase more sodic, olivine absent. - Interstitial quartz may occur.	Tholeiite and alkaline
				<i>Rhyolites</i>	
				- Phenocrysts of plagioclase, pyroxene and opaques, occasionally alkali feldspar - Groundmass: quartz and alkali feldspar are common with Ca-rich clinopyroxene, pigeonite, Ti-magnetite and ilmenite	
Pl: plagioclase; ol: olivine; agt: aegirine-augite; hd: hedenbergite; cpx: clinopyroxene; au: augite; pi: pigeonite; Ti-mat: titanomagnetite; opx: orthopyroxene; chx: chromite; amph: amphibole; qz: quartz; bi: biotite;					
*Absence of the high-k calc-alkaline and shoshonitic series					

3.2.2. Deleterious constituents of volcanic rocks

It is known from the literature on ASR (Sims and Nixon, 2003b; RILEM AAR-1.1, 2016; Fernandes et al., 2016) that different forms of silica present in volcanic aggregates have been considered responsible for the occurrence of ASR in concrete (e.g. microcrystalline or cryptocrystalline quartz, cristobalite, tridymite, opal, chalcedony and siliceous volcanic glass). Alexander and Mindess (2005) consider not only silicic to intermediate silica-rich volcanic glass potentially reactive but also basic volcanic glass and devitrified glass.

Quartz, cristobalite, tridymite, chalcedony and opal are all forms of silica. Cristobalite and tridymite are polymorphs of silica with the same composition as quartz but with different crystalline structures; quartz crystallizes in the hexagonal crystal system while the other two

crystallize in the tetragonal and orthorhombic crystal systems, respectively. Regarding volcanic glass, it has a variable chemical composition where it can range from basic to acid in terms of SiO_2 content. Opal is a hydrated form of silica and chalcedony is a crypto- to the microcrystalline, fibrous form of quartz.

Quartz

Quartz is a major constituent and one of the purest minerals on earth. There are α -quartz and β -quartz that are considered silica polymorphs. Most of the silica occurs as α -quartz due to its stability in the pressure and temperature field. At ambient pressure, α -quartz is transformed to β -quartz above 573°C , while β -quartz is transformed into tridymite above 867°C and cristobalite above 1470°C ; when cooled, the melt crystallizes as cristobalite and then into tridymite below 1470°C and further cooling leads to α -quartz at 573°C (Broekmans, 2004).

Petrographically, quartz is colourless with low relief and interference colours of the first order from grey to white with a slight tinge of white (Kerr, 1977). According to Katayama et al. (1989), quartz appears as rounded patches of sponge-like aggregates with uniform extinction in a poorly crystallized matrix of slightly altered volcanic rocks.

Quartz occurs in rocks such as sandstones, quartzites, granites, gneisses and rhyolites. It also appears as a secondary mineral in seams and cavities of different igneous rocks (Kerr, 1977). According to Demange (2012), quartz is one of the silica polymorphs that crystallizes in the early stages of the evolution of magma at depth, forming phenocrysts usually euhedral bipyramidal phenocrysts and showing frequent embayments due to the reaction with the magma. In basalts, quartz is found in the interstitial mesostasis (Tiecher et al., 2018). Sometimes, quartz forms xenocrysts, as stated by Cox et al. (1979) and xenocrysts of quartz grains are derived from sandstone wall rocks in alkali basalt. Also, Medeiros (2011) identified a xenocryst of quartz in a trachybasalt rock from São Miguel Island, Azores. Quartz is usually not present in rocks containing feldspathoids (e.g. leucite, nepheline, sodalite), being considered incompatible with feldspathoids. Cox et al. (1979) stated that nepheline and quartz, leucite and quartz, do not co-exist in equilibrium in normal rocks.

Broekmans (2004) indicates that quartz is by far the most occurring silica polymorph in alkali-reactive aggregate materials. Micro- or cryptocrystalline as well as strained quartz is considered potentially alkali-reactive (RILEM AAR-1.1, 2016). According to Deng et al. (2004), some reactive rhyolites from China contain in their matrix micro- or cryptocrystalline quartz and also minor quantities of chalcedony. In India, basalt from the Deccan plateau was considered reactive due to the presence of chalcedony and cryptocrystalline quartz (Yamada and

Miyagawa, 2017). Also, a reactive basalt from western India is reported in Mullick (2017) due to the presence of strained quartz. Shayan and Freitag (2017) refer to reactive dacite containing microcrystalline quartz and strained quartz in the matrix.

Cristobalite and tridymite

Under the microscope, both silica polymorphs show some similarities and differences between each other. Cristobalite is colourless and depending on the temperature of formation it can be practically isotropic (below 1470°C) or have grey interference colours (higher than 1470°C), resulting in a characteristic mosaic effect (Poole and Sims, 2016). Tridymite is also colourless but with wedged or arrowhead crystals but also in the form of laths (Poole and Sims, 2016). It occurs also in lithophysae structures (Kerr, 1977).

According to Katayama et al. (1989), tridymite typically occurs as coarse mosaics in the interstices of the andesite groundmass but occasionally forms wedge-shaped plates in the cavities of the rock. The same authors indicate that tridymite can occur as slender platelets parallel to the flow texture or delimited by glass altered to smectite clay. Tridymite is more common than cristobalite and is present in the cavities of acid and intermediate volcanic rocks (rhyolite, trachyte, andesite) and less frequently in basalt (Selley et al., 2005; Nesse, 2004; Poole and Sims, 2016). Cristobalite occurs in volcanic rocks such as obsidian, rhyolite, andesite and basalt (Kerr, 1977). It is usually found in cavities associated with tridymite and other minerals and can form spherulites with intergrown feldspar fibers or be part of the fine-grained groundmass (Nesse, 2004) as small pools (Poole and Sims, 2016). Broekmans (2004) indicates that the devitrification of volcanic siliceous glass leads to the formation of cristobalite/tridymite intergrowths. According to Katayama et al. (1989), cristobalite occurs in basalts and andesites as: (1) fine mosaic aggregates, intergrown with microlites of feldspar and pyroxene in the groundmass or (2) rounded patches with a roof tile texture. One of the features of cristobalite is a characteristic peculiar curve fracture (Kerr, 1977) that resembles overlapping roof tiles (Katayama et al., 1989; Sims and Poole, 2016), while tridymite is the twinning and the wedge-shaped sections. Cox et al. (1979) stated that certain volcanic rocks of the calc-alkaline suite, especially the two-pyroxene andesites from island arc volcanoes, contain interstitial silica minerals that occur as late crystallization in the form of tridymite and cristobalite. However, cristobalite can be difficult to detect in basalts, as stated by Sims and Poole (2016).

Regarding the reactivity of both silica polymorphs, Kennerley and St John (1988 in Poole and Sims, 2016) stated that it is only needed as little as 2% of cristobalite to consider the

aggregate as potentially reactive and hence causing damage in concrete (Poole, 2017); Poole (2017) states that small percentages of tridymite can cause an expansion in concrete. In Cheju Island (South Korea), there is a report of a silica-rich tholeiite basalt where ASR damage was associated with the presence of cristobalite (Yamada and Miyagawa, 2017). Andesite from Hokkaido was investigated from the point of view of ASR and it was considered deleterious due to the presence of tridymite (Yamada et al., 2014). In Japan, volcanic rocks such as andesite and some rhyolites that contain cristobalite/tridymite and acid glass are considered reactive (Yamada and Miyagawa, 2017). Katayama et al. (1989) affirm that the amount of silica minerals detected by the phosphoric acid method is significantly higher when compared to what is observed under the microscope; the authors suggest that the silica minerals are present as a finely divided form in the groundmass and could be considered highly reactive. According to Broekmans (2004), cristobalite and tridymite are thermodynamically less stable than quartz and therefore more prone to dissolution and/or alkali reactivity than quartz.

Chalcedony

Chalcedony is a finely crystalline form of quartz. It is considered a fibrous type of cryptocrystalline quartz (Haldar and Tišljär, 2014; Poole, 2017). Chalcedony was known before as a distinct mineral, but electron microscopy has shown that it is formed by minute quartz crystals (Poole and Sims, 2016).

Under the microscope it is colourless to pale brown and often shows a radial, mosaic or banded structure but also takes frequently takes a spherulitic form. Like opal, chalcedony appears to replace organic structures at the cellular level and in general as microfossil replacement (Kerr, 1977). It occurs as secondary material in cavities of igneous rocks (Kerr, 1977) in the form of geodes or agate (Nesse, 2004) and it is the main constituent of cherts and flints (Poole, 2017). It is often associated with crystalline quartz, opal and zeolites (Kerr, 1977).

Regarding its potential reactivity, chalcedony together with other forms of silica is considered potentially reactive (Alexander and Mindess, 2005). In Iceland, the high reactivity of some basalts is assumed to be due to the presence of chalcedony and secondary opal, together with primary cristobalite and rhyolitic glass (Katayama et al., 1996). Also, basalt from the Deccan plateau in India included chalcedony and cryptocrystalline quartz as reactive minerals (Yamada and Miyagawa, 2017). Deng et al. (2004) also reported a reactive basalt with 3% to 5% of chalcedony present in the rock. However, according to Poole and Sims (2016), the presence of submicroscopic chalcedony does not necessarily indicate potential

reactivity. According to Poole (2017), moderate alkali reactivity happens in some cases, but it depends on the composition and structure of chalcedony.

Opal

Opal is amorphous to slightly crystalline (Dutkiewicz et al., 2015) hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) with variable amounts of water (1 to 21%) (Haldar and Tišljär, 2014), commonly between 4%-9% (Poole and Sims, 2016) of sedimentary opals and between 9-18% of volcanic opals (Smallwood et al., 2008; Dutkiewicz et al., 2015). According to Dutkiewicz et al. (2015), opal is commonly referred to as “sedimentary opal” and “volcanic opal”, which is derived from sedimentary and volcanic environments, respectively (Smallwood et al., 2008). Therefore, opal occurs in different rocks and is usually found in basalt, rhyolite, sandstone and marl (Haldar and Tišljär, 2014) and occurs commonly associated with quartz, chalcedony and tridymite (Kerr, 1977; Poole and Sims, 2016). According to Kerr (1977), fossil diatoms and other microscopic remains are usually composed of opal and when it replaces wood frequently exhibits their cellular structure; it replaces also feldspar. It is considered a secondary mineraloid in volcanic rocks and appears usually in cavities or seams.

Jones and Segnit (1971) studied different opals by X-ray diffraction; the authors subdivided opal into three well-defined structural groups: (1) Opal C, well ordered α -cristobalite; (2) Opal CT, disordered α -cristobalite, α -tridymite and (3) Opal A, highly disordered, near amorphous. According to Dutkiewicz et al. (2015), volcanic opal is classified as opal CT, a partially crystalline opal. In Australia, volcanic opal, a precious opal, is associated with a decomposed basalt from Lismore Basalt and part of the Lamington Volcanics of the Miocene age (Smallwood et al., 2008).

In terms of petrographic characteristics, opal is isotropic and colourless to pale grey or brown in thin sections; in the case of gem opals, they show a play of colours (Kerr, 1977; Nesse, 2004). In the presence of impurities, the colour changes to yellow, grey, brown or red (Haldar and Tišljär, 2014). Regarding the forms, opal is usually banded or with colloform structures and can also be present in cellular organic structures or as a replacement for microfossils (Kerr, 1971).

Opal is usually highly alkali-reactive (Alexander and Mindess, 2005), and is considered one of the most reactive forms of silica (Smith and Collins, 2001). Highly reactive forms such as opal may require as little as 2 % to cause deleterious expansion; this is known as the pessimum phenomenon that occurs with certain rapidly reacting forms of silica (Alexander and Mindess, 2005). One example of deleterious expansion was reported in a railway bridge concrete from

Japan where andesite that contained opal veins were used as concrete aggregates. The petrographic examination concluded that opal was the cause of the concrete damage (Yamada and Miyagawa, 2017). In Australia, Shayan and Quick (1988) and Shayan (2004) refer to an alkali-reactive basalt due to its opaline components.

Volcanic glass

Some volcanic glasses are considered reactive (rhyolitic glass, hydrated rhyolitic glass) as well as devitrified volcanic glass (Sims and Nixon, 2003). Katayama et al. (1989) also consider rhyolitic glass as potentially reactive. Alexander and Mindess (2005) classify all the glasses (rhyolitic and basic compositions) as reactive components as well as palagonite. The recommendation of RILEM AAR-1.1 (2016) attributes the reactivity of volcanic glass to its amorphous, non-crystalline structure; the devitrified/altered/hydrated glasses are also known to be prone to deleterious ASR.

Volcanic glass is an amorphous material formed from a rapidly cooling melt that did not have time to crystallize. It comes from silicate magmas and can range in composition from basaltic to rhyolitic. The formation of volcanic glass is dependent on the rate of cooling and the chemical composition of the lava (Bailey, 1989). It seems that no volcanic glasses are known with less than 35% or more than 80% of silica (Beal, 1981), although some early analyses made by George (1924) showed that volcanic glass can reach 82% in silica content. According to Beal (1981), the chemical distribution according to the silica content exhibits a dominant peak at about 73% of silica, which corresponds to rhyolitic glass; the same happens with basaltic glass for which there is a maximum peak at about 52% of silica.

Glass can either create an individual rock type or it can be present in the groundmass of different volcanic rocks (Kerr, 1977). According to George (1924), volcanic glasses are named based on composition and structure. Some of these glasses are known as: *obsidian*, a felsic silica-rich glass (70-76 wt% silica content) with 0.1-2.5 wt % of water (Glass, 2016); *perlite*, a highly hydrated glass rock of rhyolitic composition, which contains many spherical cracks (Dehn and McNutt, 2015) and has a water content higher than obsidian (Ewing, 1979); *pumice*, a vesicular rich volcanic glass that ranges between intermediate to felsic composition (~55-75wt% silica content) and with a density less than 1 g/cm³ that allows to floating on water (Dehn and McNutt, 2015; Glass, 2016); *tachylite* and *sideromelane*, both are mafic glasses with water content between ~0.1-1.0 wt % (Glass, 2016).

The occurrence of interstitial volcanic glass or devitrified volcanic glass is a common feature of the groundmass of volcanic rocks (Cox et al., 1979). Bailey (1989) states that volcanic glass

is more usually found in rocks such as rhyolites and dacites than in basalts and andesites. Beal (1981) also points out that rhyolite glass seems to be about three times more abundant than basalt or andesite glass. This is probably due to what Glass (2016) affirms: felsic lava takes time to crystallize and can form larger masses of glass than mafic lavas. Also, Gifkins et al. (2005) sustain that there is a higher proportion of glass in felsic volcanic facies than in mafic facies. Friedman and Long (1984) stated that this happens because of the viscosity of silicic magmas that inhibits diffusive crystal growth. The opposite happens to basaltic magmas because their low viscosity favours crystallization. According to Glass (2016), the type of volcanic glass is determined by the composition of the magma and the type of eruption, which are related to the geological setting where they occur. For example, in subduction settings, the groundmass or matrix glass in porphyritic andesites and dacites is invariably rhyolitic in composition (Annen et al., 2006).

Volcanic glasses have limited durability in time and they are considered thermodynamically unstable (Bonatti, 1965; Friedman and Long, 1984; Fisher and Schmincke, 1984; McPhie et al., 1993; Winter, 2001; Gifkins et al., 2005). However, Friedman and Long (1984) refer to some samples of glass found with 60 Ma and with no alteration. In general, volcanic glasses are more susceptible to alteration when compared to minerals because they lack well-developed crystal structures and therefore will devitrify, dissolve or alter to minerals (Gifkins et al., 2005). Even between glasses, mafic glasses are more rapidly altered than felsic glasses (Fisher and Schmincke, 1984; Friedman and Long, 1984). It seems that the rate of alteration is connected to the chemical composition of the glass and the temperature (Friedman and Long, 1984). Therefore, the increase in SiO_2 decreases the rate of alteration while the increase of MgO , CaO and water increases the rate of alteration (Gifkins et al., 2005). Friedman and Long (1984) sustain that rhyolite glass is more stable than basaltic glass. The reason for that is related to its viscosity and low content in water and at temperatures less than 600°C , which allows that rhyolitic glasses do not devitrify with time. The same authors also emphasize that the glass will devitrify quickly if it contains a certain amount of water. It seems also that volcanic glass alters in the presence of alkaline fluids and by being exposed to elevated temperatures; however, the alteration is reduced under dry conditions or in the presence of pure water (Lofgren, 1970 in Gifkins et al., 2005). Generally, volcanic glass tends to alter to different products with time. Based on the work of different authors, Gifkins et al. (2005) summarized in a table the common alteration minerals that replace the glass of silicic and mafic nature. The authors show that for silicic volcanic glass, the alteration products are: zeolites (mordenite, clinoptilolite, laumontite, analcime, heulandite), cristobalite, opaline silica, quartz, calcite and clays (montmorillonite, smectite, mixed-layer clays). In the case of mafic volcanic glasses, the

alteration products are: palagonite, nontronite clay minerals, smectite, calcite, chlorite, epidote, Ca-rich zeolites and Fe/Ti/Mn-oxides. Devitrification is the most common form of alteration in natural glass and is referred to as the crystallization of glass (Gifkins et al., 2005; Gill, 2010) or the secondary crystallization of glass (Winter, 2001). According to Kerr (1977), volcanic glass is often more or less devitrified and the alteration products are usually indefinite; however, feldspar, tridymite, cristobalite or montmorillonite are sometimes the results of the devitrification. Also, Winter (2001) affirms that the acidic volcanic glass turns into a microgranular mass of small grains of interlocking feldspar and silica minerals, while basaltic glass devitrifies into palagonite, a yellow or orange isotropic mineraloid.

Kerr (1977) included volcanic glass and palagonite in the group of mineraloids because they do not have a fixed chemical composition or crystal structure to be defined as a mineral. However, Tiecher et al. (2012) consider that volcanic glasses the majority of the time are not amorphous and are instead formed by crypto-microcrystalline mineral phases: mesostasis. According to Peacock (1926), there are two varieties of palagonite: an amorphous (gel) palagonite and a poorly crystalline fibro-palagonite. For Stroncik and Schmincke (2002), the two varieties of palagonite defined by Peacock (1926) are nothing more than different evolutionary stages that range from purely amorphous (palagonite), passing through a mix of palagonite and crystalline phases and mainly crystalline up until fully crystalline (smectite).

Under the microscope, volcanic glass is isotropic. It is usually colourless to grey or reddish (Kerr, 1977), sometimes brown or greenish in colour (Cox et al. 1979). For example, sideromelane shows a clear light brown colour and tachylite is dark brown to opaque (Glass, 2016), partly or completely charged with microlites of FeTi-oxide (ilmenite and titanomagnetite). According to George (1924), the black and brown colours in volcanic glass are dependent on the presence of dark crystals and crystallites. Regarding palagonite, it can range in colour from yellow to shades of brown (Stroncik and Schmincke, 2002). The two varieties of palagonite defined by Peacock (1926 in Stroncik and Schmincke 2001) have different optical characteristics: (1) a gel palagonite amorphous, which is isotropic and commonly concentrically banded (Fisher and Schmincke, 1984; Stroncik and Schmincke, 2002), clear, transparent, smooth (Stroncik and Schmincke, 2002) and forming the alteration zone next to the unaltered glass (Fisher and Schmincke, 1984); (2) poorly crystalline fibro-palagonite, translucent, anisotropic, slightly to strongly birefringent material of fibrous, lath-like or granular structure (Stroncik and Schmincke, 2002).

Despite all these definitions for volcanic glass and its alteration products, it is essential in ASR-related investigations to identify firstly by microscope which components of the rocks are causing the problems, volcanic glass being one of these deleterious components.

CHAPTER 4

METHODS AND MATERIALS

4.1. Materials

Several aggregates were selected from different locations around the world to identify the characteristics of the aggregates leading (or not) to the occurrence of deleterious internal reactions due to ASR. The present study includes volcanic rocks of basic, intermediate and acid composition. The first type of rock is the focus of this research (e.g. basalts), while the others are included in the study mainly for control purposes (e.g. andesite and rhyolite).

The aggregates come from different countries with distinct geological environments (Figure 4.1): Brazil, Canada, Iceland, Japan, Mozambique, New Zealand, Norway, Portugal (Azores and Madeira Archipelagos), Spain (Canary Islands), Turkey and the United States (Hawaiian Islands). Table 4.1 summarizes the aggregate samples per country and the code attributed to each one.

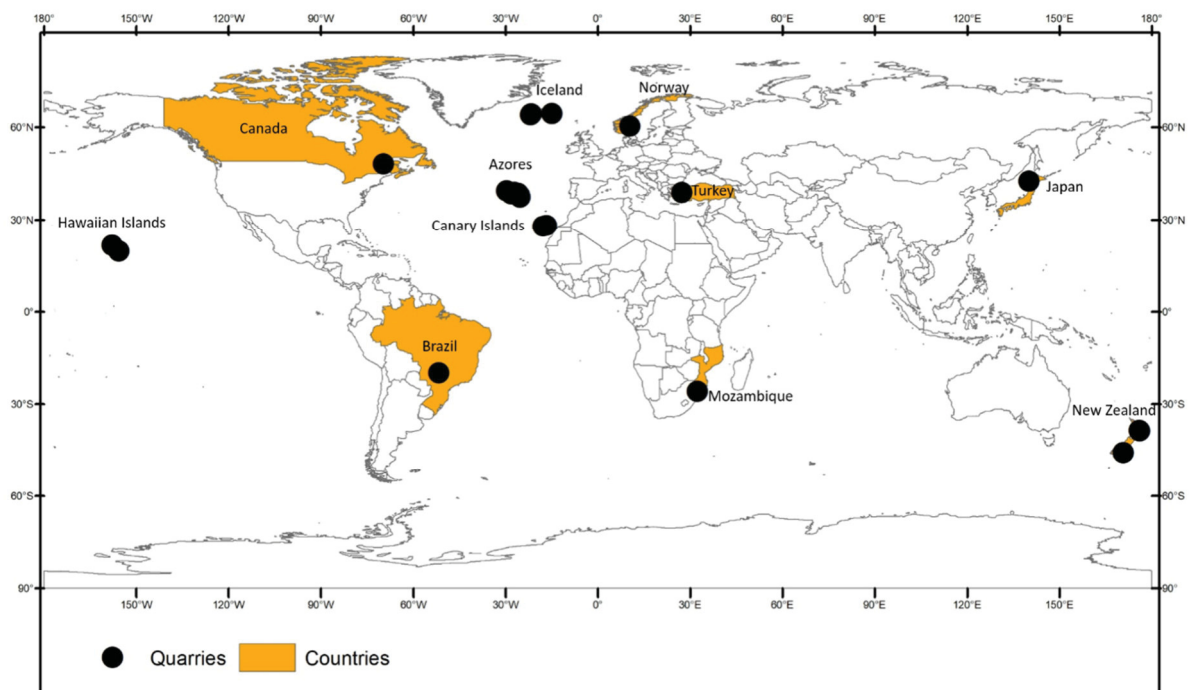


Figure 4.1. Map view of the origin of the selected aggregate samples: Azores (all islands); Brazil (Ilha Solteira); Canada (near Québec city); Canary Islands (Tenerife and El Hierro Islands); Iceland (Western and Southeastern areas); Japan (Western Hokkaido); Mozambique (Karoo area); New Zealand (North and South Islands); Norway (Near Oslo); Turkey (near Aliağa).

Table 4.1. Aggregate samples per country. Materials tested correspond to coarse aggregates, except when “sand” is mentioned.

Country	Sample	Mineralogical name (Sims and Nixon, 2003b)
Brazil	BRAZ	Basic volcanic rock
Canada	CAN	Basic volcanic rock
Iceland	ICL1	Gravel (Basic/acid volcanic rock)
	ICL1 fine sand	Gravel (Basic/acid volcanic rock)
	ICL1 coarse sand	Gravel (Basic/acid volcanic rock)
	ICL2	Gravel (Basic/acid volcanic rock)
	ICL3	Basic volcanic rock
	ICL3 sand	Basic volcanic rock
	ICL4	Gravel (Basic/acid volcanic rock, mafic rock)
	ICL4 sand	Gravel (Basic/acid volcanic rock, mafic rock)
Japan	JAP	Intermediate volcanic rock
Mozambique	MOZ	Acid volcanic rock
New Zealand	NZ1	Ultrabasic volcanic rock
	NZ2	Basic volcanic rock
	NZ3	Basic volcanic rock
Norway	NOR	Basic volcanic rock
Portugal (Azores)	SMA-SM1	Ultrabasic volcanic rock
	SMA-SM2	Ultrabasic volcanic rock
	SMG-SM1	Basic volcanic rock
	SMG-SM2	Basic volcanic rock
	SMG-SM3	Basic volcanic rock
	TER-SM1	Acid volcanic rock
	TER-SM2	Basic volcanic rock
	GRA-SM1	Basic volcanic rock
	SJO-SM1	Basic volcanic rock
	PIC-SM1	Basic volcanic rock
	FAI-SM1	Basic volcanic rock
	FLO-SM1	Intermediate volcanic rock
	FLO-SM2	Intermediate volcanic rock
	CRV	Basic volcanic rock
Spain (Canary Islands)	CANY1	Ultrabasic volcanic rock
	CANY2	Ultrabasic volcanic rock
Turkey	TK	Intermediate volcanic rock
USA (Hawaiian Islands)	HW1	Basic volcanic rock
	HW2	Basic volcanic rock
	HW3	Basic volcanic rock
	HW4	Intermediate volcanic rock
	HW5	Basic volcanic rock
	HW6	Basic volcanic rock
	HW7	Basic volcanic rock
	HW7 sand	Basic volcanic rock

The aggregates from Azores Archipelago were partly studied by Medeiros (2011). The petrographic examination on five aggregate samples was carried out and only for one of the samples the mortar bar test (AMBT-ASTM C 1260) and the accelerated concrete prism test (RILEM AAR-4.1) were performed. Between 2012 and 2016, all the Azorean aggregates were investigated within the scope of the ReAVA and IMPROVE research projects. Petrographic examination and laboratory tests (e.g. mortar bar and concrete prism tests) were performed for all of the aggregate samples. Only one of the islands was not included in the above-mentioned studies due to the lack of local aggregate exploitation. However, recently, an exploitation area was created for construction purposes. This new aggregate was included in the present work.

Most of the samples studied in this research come from conventional bedrock quarries (crushed aggregates). There are some exceptions where the aggregates extracted are not coming from quarries. This was reported in Medeiros et al., (2016) for Flores Island (Azores) where: (1) one of the aggregate samples was taken from a river nearby and then crushed for concrete manufacturing purposes and (2) the other one was extracted from an excavation site. There is also the case of the gravels from Iceland that are exploited either from sea-dredged areas or from materials extracted from a beach, both composed of heterogeneous material of a variety of rock types (e.g. basalt, altered basalt, rhyolite, dacite).

In this study, other aggregates were used exclusively for the expansion tests, where no petrographic examination was done. These aggregates are the control materials and the fine aggregates (e.g. volcanic sands) (Table 4.2). The Spratt and the GBS sand were used as references for the laboratory tests (AMBT and CPT). Spratt is a reactive siliceous limestone aggregate from a quarry near Ottawa, Canada. It has been used as a control material for several ASR studies. It is referenced by CSA A23.2-14A (2015) and RILEM AAR-0 (2016). GBS is a coarser sand of basaltic nature from Iceland, where 40% corresponds to basaltic glass. According to the producer, it is considered innocuous but in the present work, it showed some reactivity. The fine aggregates include some sands of basaltic nature from the Hawaii Islands (HW7 sand) and from Iceland (ICL1 fine sand, ICL1 coarse sand, ICL3 sand, and ICL4 sand) that were used in the mortar bar and the concrete mixes. These aggregates were mixed with a non-reactive fine or coarse aggregate (a high-purity limestone - HP), depending on the test method, to evaluate their behavior. In addition, one of the mixes for the CPT incorporated the coarse and fine aggregate from the same source to evaluate its performance.

The majority of the aggregates were subjected to a series of methods (e.g. petrographic examination, laboratory expansion tests) described in the subchapter *Methods*. It is intended

to follow the assessment scheme for the potential ASR recommended by RILEM AAR-0 (2016) with the help of supplementary methods, some of them being described in Sims and Nixon (2003b) (e.g. Scanning electron microscopy, Phosphoric acid method, Gel-Pat Test).

Table 4.2. Aggregates are used exclusively in the AMBT and CPT.

Aggregates	Type
Spratt	Reactive siliceous limestone from Canada
GBS sand	coarser sand from Iceland
HW7 sand	Sand from the island of Hawaii
ICL1 fine sand	Sea-dredged fine sand from Iceland
ICL1 coarse sand	Sea-dredged coarse sand from Iceland
ICL3 sand	Sand from a quarry in Iceland
ICL4 sand	Sand extracted from a beach in Iceland

4.2. Methods

The assessment of the potential alkali reactivity is carried out through a series of standard methods (ASTM, CSA) and by the RILEM recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures. The recommendation of RILEM AAR-0 (2016) indicates that either new or existing sources of concrete aggregates should be assessed before being used in concrete applications. It also states that the evaluation of potential ASR should not be carried out alone but rather as a specialized extension to the routine assessment of the suitability of an aggregate. The ASR assessment should follow the principles illustrated in the same recommendation by using different methods (Figure 4.2): (1) petrographic examination that classifies the aggregate into 3 classes (I. unlikely to be alkali-reactive, II. uncertain and III. very likely to be alkali-reactive); (2) a rapid screening test (Accelerated mortar bar test – AAR-2) that gives a rapid result; (3) concrete expansion testing (AAR-3 and AAR 4.1) for assessing combined aggregates. This recommendation also points out that it is imprudent to rely merely on the results of the accelerated screening tests and the results should always be confirmed by one of the concrete prism tests.

Swamy (1992) assumed that a combination of petrographic studies, a field performance survey and a concrete prism test is recommended for assessing the potential alkali-reactivity of aggregates.

Nixon and Fournier (2017) state that ASTM, CSA and RILEM all recommend a methodology based on the following three stages: 1) petrographic examination, 2) screening using an accelerated mortar-bar test and 3) longer-term testing using concrete specimens.

A SWOT analysis was done for the methods presented in the three stages and also for the Gel Pat Test and the DRI methods. This analysis has the purpose of showing the strengths, weaknesses, opportunities and threats of each method.

The importance of each method is described in the following subchapters.

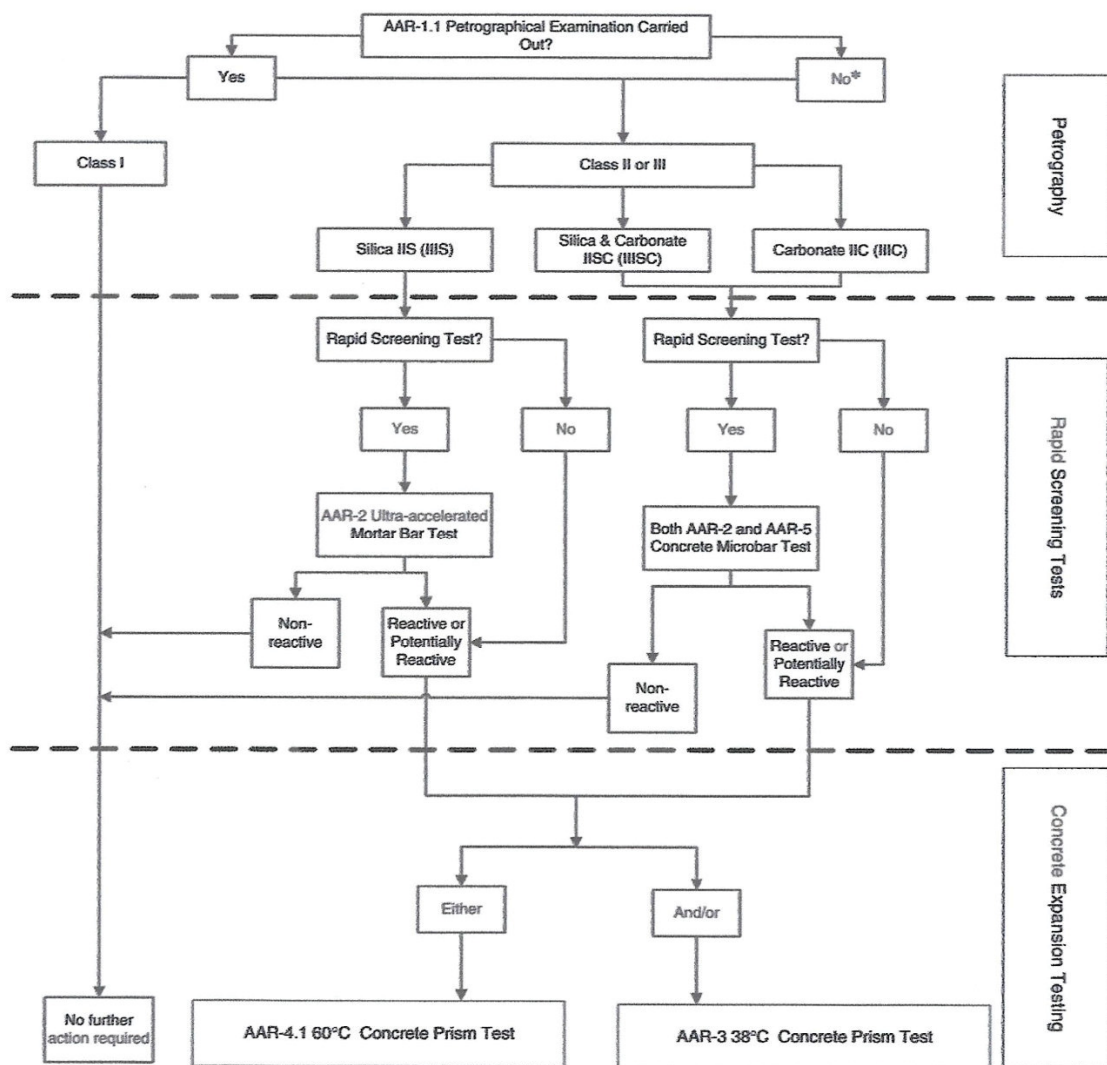


Figure 4.2. Integrated assessment scheme for the potential ASR (RILEM AAR-0, 2016).

4.2.1. Aggregates

Petrographic Examination

Petrography is a branch of geology that studies the mineralogical composition and texture, gives information about the order of crystallization of minerals and classifies a rock, all that by the examination of a thin section under a polarizing microscope. Petrography relies heavily on observations made with the petrographic microscope (Philpotts, 1990).

Since the 1800s, thin section analysis of rocks using a polarizing microscope has been a traditional tool of the geologist (Welton, 2003). Nowadays, the polarizing microscope is used not only for rocks but also for the examination of concrete and related materials. Geomaterial engineers, for example, use the polarizing microscope to examine thin sections or polished surfaces of samples in the same way that geologists examine rock samples (Ingham, 2011). The petrographic examination of aggregates is done for different purposes. Table 4.3 lists the petrographic purposes in some of the international standards ASTM C 295 (2019), EN 932-3 (2010), the RILEM recommendation AAR-1.1 (2016) and also according to Blight and Alexander (2011) and Ingham (2011). Other national standards include CSAA23.2.15A (2009) and the Portuguese specification LNEC E 415 (1993). The principles and methods to use are common amongst these standards, although some are more specific than others.

Petrographic examination is one of the most important methods for evaluating ASR and according to RILEM AAR-0 (2016), it should always be the first step to assess the alkali-reactivity of concrete aggregates. This analysis identifies the potentially reactive constituents present in the rocks (Table 4.4). Nixon and Fournier (2017) also mention that petrographic examination is a powerful method to identify different types of siliceous phases in the aggregate. However, it depends on the experience and skills of the petrographer. According to RILEM AAR-0 (2016), the petrographic analysis should be carried out by a qualified geologist with experience in materials used for concrete and with a good knowledge of the local aggregates considered alkali-silica reactive. Also, ASTM C 295/295M (2019) states that to conduct petrographic examination on aggregates for concrete, the petrographer should have completed college-level course work about basic geology, mineralogy, petrography and optical mineralogy or have obtained equivalent knowledge through experience and on-the-job training and also some years of experience. The Canadian standard A23.2-15A states that the petrographic examination should be performed by persons who are qualified by both education and experience. EN 932-3 (2010) remarks that the petrographic analysis should be performed by a specialized geologist (petrographer) with experience in materials used in civil engineering.

Similarly, the specification LNEC E 415 (1993) states that the petrographic analysis should be done by a petrographer with ASR knowledge and experience in analytical routines.

Table 4.3. Purpose of the petrographic examination of aggregates as in international and national standards, specifications, recommendations and according to Blight and Alexander (2011) and Ingham (2011).

Standard/Specification	Purpose of petrographic examination of aggregates
A23.2.15A (2014) Petrographic examinations of aggregates	• Determine the physical and chemical characteristics of the aggregates that can have a bearing on the performance of the material in its intended use; • Describe, classify and determine the relative amounts of constituents of the aggregate; • Compare samples of aggregates from new or proposed sources with samples of aggregates from other sources for which test data or performance records are available; • Identify harmful characteristics or undesirable components of aggregates specific to their intended use.
ASTM C295/C295M (2019) Petrographic Examination of Aggregates for Concrete	• Determine the physical and chemical characteristics of the material that may be observed by petrographic methods and that have a bearing on the performance of the material in its intended use; • Describe and classify the constituents of the sample; • Determine the relative amounts of the constituents of the sample that are essential for proper evaluation of the sample when the constituents differ significantly in properties that have a bearing on the performance of the material in its intended use; • Compare samples of aggregate from new sources with samples of aggregate from one or more sources, for which test data or performance records are available.
EN 932-3 (2010) Procedure and terminology for the simplified petrographic description	• Describe the type of aggregate and its physical characteristics; • Classify the aggregate.
LNEC E 415 (1993) Determination of the potential reactivity with the alkalis. Petrographic examination	• Describe the type of aggregate and its physical characteristics; • Classify the aggregate; • Identify specially the aggregates and minerals with potentially reactive forms of silica.
RILEM AAR-1.1 (2016) Petrographic examination method	• Identify the rock types and minerals that might react with hydroxyl ions from the concrete pore solution.
Blight and Alexander (2011)	• Describe aggregate constituents and determine their relative amounts, permitting classification; • Determine certain physical and chemical characteristics that may influence the performance of the aggregate in concrete; • Detect potentially deleterious constituents or undesirable minerals and contaminants in the aggregates such as sulphates, as well as the presence of aggregate coatings; • Establish the likely performance of aggregates from new or untried sources by comparing their characteristics with aggregates of known performance; • Assist in interpreting results of other standard aggregate tests and in selecting further tests for determining aggregate performance.
Ingham (2011)	• Initial suitability assessment of aggregates from new sources; • Routine quality assurance of aggregate from the production run; • Matching aggregate types for restoration of mortar in historic buildings; • Assessing the potential alkali-aggregate reactivity in concrete.

The potential alkali-reactivity of the same rock type may vary from country to country, even from different sources within the same country. According to Fernandes et al. (2015), the distinction between innocuous and potentially reactive aggregates depends on the type of silica present and its geological history. A single geological nomenclature is no longer sufficient because the geological history and the mineralogical and textural aspects of a given rock type have a huge influence on concrete (Fernandes et al., 2012). RILEM AAR-1.1 (2016) also indicates that reactive constituents differ between countries.

Table 4.4. Rock types and potentially alkali-reactive constituents of each rock type according to RILEM AAR 1.1 (2016).

Rock type	Potentially alkali-silica reactive constituents
Andesite	silica polymorphs cristobalite and tridymite, interstitial glass in the matrix, or devitrified glass, opaline silica or chalcedony from low-temperature alteration.
Argillite, Argillaceous	microcrystalline quartz.
Basalt	silica polymorphs cristobalite and tridymite, interstitial glass in the matrix, or devitrified glass, opaline silica or chalcedony.
Chert, Flint	chalcedony, opal, cryptocrystalline and/or microcrystalline silica
Diorite	retrogradation of pyroxene to form amphibole plus micro-crystalline quartz, or to late-stage veining.
Dolomite	Finely disseminated quartz, opal or chalcedony
Gneiss	strained quartz from (tectonic) deformation, and/or poorly (micro-, crypto-) crystalline interstitial quartz.
Granite, Granodiorite	strained quartz from deformation (rather common along intrusive margins), or poorly (micro-, crypto-) crystalline quartz.
Granulite	strained quartz by deformation, or poorly (micro-, crypto-) crystalline interstitial quartz.
Greywacke	Fine-grained quartz with a large accessible surface area and/or the presence of poorly (micro-, crypto) crystalline quartz.
Hornfels	Fine-grained quartz with a large accessible surface area and/or poorly (micro-, crypto-) crystalline quartz.
Limestone, Chalk, Marl	Fine-grained and poorly (micro-, crypto-) crystalline silica.
Mudstone	fine-grained and/or poorly (micro-, crypto-) crystalline quartz
Mylonite, Pseudotachylite, Fault Breccia/Gouge, Cataclasite	strained quartz, glass matrix (pseudotachylite), and/or very fine-grained and poorly (micro-, crypto-) crystalline silica from tectonic crushing.
Quartzite	deformed-strained quartz, and/or the presence of very fine-grained and poorly (micro-, crypto-) crystalline silica along grain boundaries or interstitial silica.
Rhyolite	silica polymorphs cristobalite and tridymite, interstitial glass in the matrix, or devitrified glass, opaline silica or chalcedony from low-temperature alteration
Sandstone, Siltstone	clastic constituents that are themselves reactive, to very fine-grained quartz and/or the presence of poorly (micro/crypto) crystalline quartz.
Slate	fine-grained (micro/crypto) crystalline quartz.
Tuff	presence of siliceous glass or devitrified glass, cristobalite or tridymite, poorly (micro-, crypto-) crystalline quartz. Opal and/or chalcedony.

The EU PARTNER project evaluated several tests developed by RILEM and also some regional tests for the suitability of aggregates across Europe (Lindgård et al., 2010). For the

petrographic method, the study performed among different laboratories showed that the degree of alkali-silica reactivity varies a lot, probably due to the experience or inexperience of the petrographer in a particular rock-type (Lindgård et al., 2010).

The recommendation from RILEM AAR-1.1 (2016) specifies a general procedure for the petrographic examination of concrete aggregates to identify the rocks and minerals considered deleterious from the point of view of ASR. In this recommendation, the aggregates are classified according to three classes:

- I. unlikely to be alkali-reactive,
- II. uncertain,
- III. very likely to be alkali-reactive.

In this recommendation, the techniques and instruments used to identify the rock types and their mineral constituents from the point of view of ASR are described. The petrographic examination is based on two techniques:

1. Macroscopic petrography: the particles from the aggregates are separated, manually, into lithological groups based on colour, mineral content, texture and morphology, etc. To aid in the particle separation, several instruments (in 4.2 from RILEM AAR-1.1, 2016) are used to identify the physical properties of minerals (hardness, streak, magnetic properties) and also a solution of hydrochloric acid is used to identify calcite and dolomite (carbonate) minerals. The binocular microscope is used in complement to the macroscopic analysis;
2. Thin-section petrography: uses an optical microscope to do point counting to know the mineral content and rock types in volume percent, when necessary.

A petrographic atlas, AAR-1.2, was developed by Fernandes et al. (2016) to complement the petrographic method described in RILEM AAR-1.1 as a guidance, and also to assist petrographers that are not familiar with reactive rocks. Among other things, this atlas identifies, by thin sections, known alkali-reactive silica types from the rock type presented and show photomicrographs of the different rocks and their reactive constituents. It also provides information regarding reactive aggregates from different parts of the world giving it a broader approach. It is detailed and very practical guidance for petrographers. Before this atlas, other documents have been published to also assist petrographers in the problem of ASR, some related to the European rocks (Lorenzi et al., 2006) and others with the Norwegian rocks (Wigum, 1999).

Petrographic examination is a quick method although the point counting method is laborious to carry out (Alaejos and Lanza, 2012). Santos Silva (2005) admits that there is an absence of a recommended value as a classification criterion, the classification is based on the content of reactive minerals identified. The acceptance and experience with reactive constituents differ among countries and should follow, whenever possible, the national or regional experiences, recommendations and specifications (RILEM AAR-1.1, 2016). Although Sims and Nixon (2003a) indicate that the petrographic examination enables any potentially alkali-reactive constituents to be identified, some reactive minerals may be difficult to identify especially in fine-grained volcanic rocks. In these cases, it is important to use supplementary methods such as SEM/EDS, XRD, phosphoric acid method, amongst others to assist the petrographer in the identification of reactive constituents in the rock.

A SWOT analysis was made for petrographic examination based on the literature described in this subchapter (Figure 4.3).

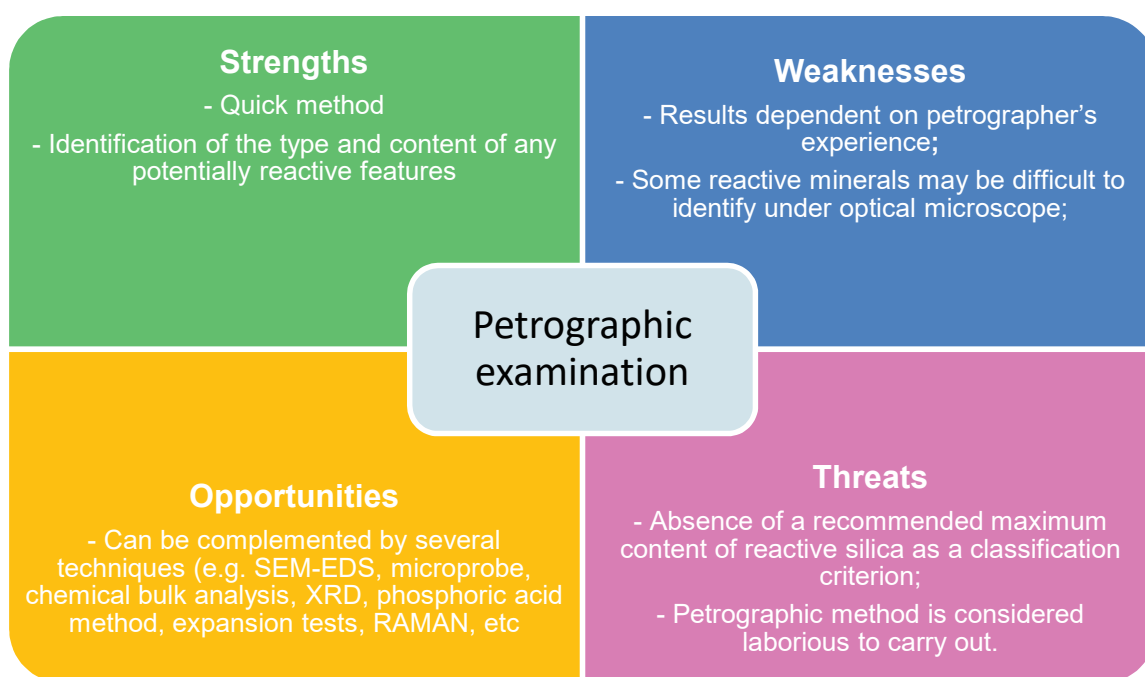


Figure 4.3. Swot analysis for the petrographic examination method.

Complementary techniques to petrography

The petrographic analysis of aggregates is sometimes complemented by other methods such as SEM-EDS, EMPA, the phosphoric acid method and chemical analysis of bulk rock. A combination of several techniques will help a petrographer in evaluating the potential reactivity of a rock. Katayama et al., (1989) indicate that knowing the bulk chemical composition of rock

together with a glass content by microscopy and silica minerals confirmed by phosphoric acid will contribute to better assessing the potential reactivity of volcanic rocks.

Scanning electron microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS)

SEM/EDS is a very important and widely used method that allows the identification and study of very small grains (Poole and Sims, 2016) that are not possible to identify with the optical microscope. It allows geologists to obtain a semi-quantitative and qualitative chemical composition and characterize the smallest minerals, and examine the distribution of these minerals within the pores and cracks (Welton, 2003). It is considered a non-destructive method.

According to Goldstein et al. (2018), some of the following information can be obtained from samples analyzed under the SEM: (1) Compositional microstructure; (2) Topography (shape); (3) Crystal structure; (4) Crystal defects; and (5) Crystal deformation effects dimension. Reed (2005) says that SEM is optimized for imaging, with analysis as an extra.

SEM is fitted with X-ray spectrometers and there are two kinds (Reed, 2005): (1) energy dispersive spectrometers - EDS and (2) wavelength dispersive spectrometers - WDS. The EDS is the most common and widely used elemental microanalysis method. EDS gives a semi-quantitative elemental analysis of the minerals being capable of identifying and quantifying most of the elements of the periodic table depending on the equipment and detector. It can give also an elemental map where the spatial distribution of the elemental constituents of a specimen is displayed and permits comparison maps of different elements in the same region, or for the same element from different regions (Goldstein et al., 2018).

SEM analysis can be done on a variety of materials (for example, core and sidewall samples, drill cuttings and thin sections) (Welton, 2005). In the case of thin sections, it can be done either on rocks or concrete. For some equipment it is required for the thin sections to be polished and then coated with a conductive metal, normally carbon is used, in a sputter coater equipment (Figure 4.4A and B) and that they fit into the sample's chamber where the sub-stage enters (Figure 4.4C). The coating (200 Å) of the thin sections should cover enough to obtain a clear image of an insulating material and should be thin enough to be able to identify the minerals (Welton, 2005). The carbon is deposited under high vacuum conditions and adheres strongly to the sample.

The scanning electron microscope (Figure 4.5) is composed of an electron optics column and an electronics console. The samples are placed in a chamber within the electron optics column and are put into a high vacuum. The SEM image is formed by an internally generated electron beam. The electrons interact with the atoms of the sample, giving information about

the surface topography (secondary electron mode) and density (backscatter mode) of the sample. An EDS spectrum is formed for each mineral and an image is shown. According to Goldstein et al. (2018), the EDS spectrum (Figure 4.6) is created in the form of a histogram in which the horizontal axis is a series of energy bins, and the vertical axis is the number of photons whose energy fits within that bin value. The peaks recognized in the energy EDS spectrum correspond to the elements assigned in the qualitative elemental analysis.

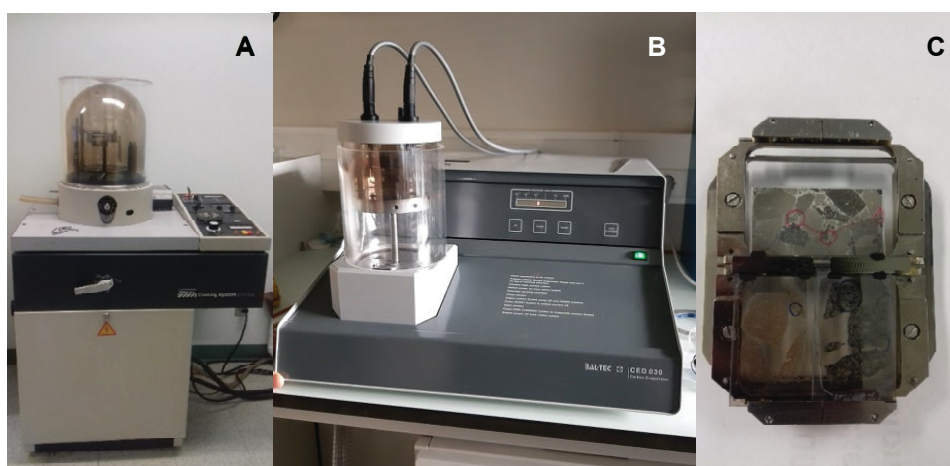


Figure 4.4. Different sputter coater equipment was used for carbon coating the samples (A and B) and (C) sample holders.



Figure 4.5. Scanning electron microscope (Laval University).

SEM has some advantages when compared to the optical microscope (Welton, 2003): (1) the samples are easy to prepare; (2) greater depth of field and resolution are obtained, and (3) a significantly higher magnification range is available (most SEM analyses of rocks involve magnifications between 10x to 20,000x). Nowadays, the magnification of the most modern SEM goes up to 300,000x (Erić, 2017).

According to Welton (2003), SEM does not replace thin-section analysis; instead, complements thin-section analysis by providing a different type of information that in combination with other techniques help to characterize rocks.

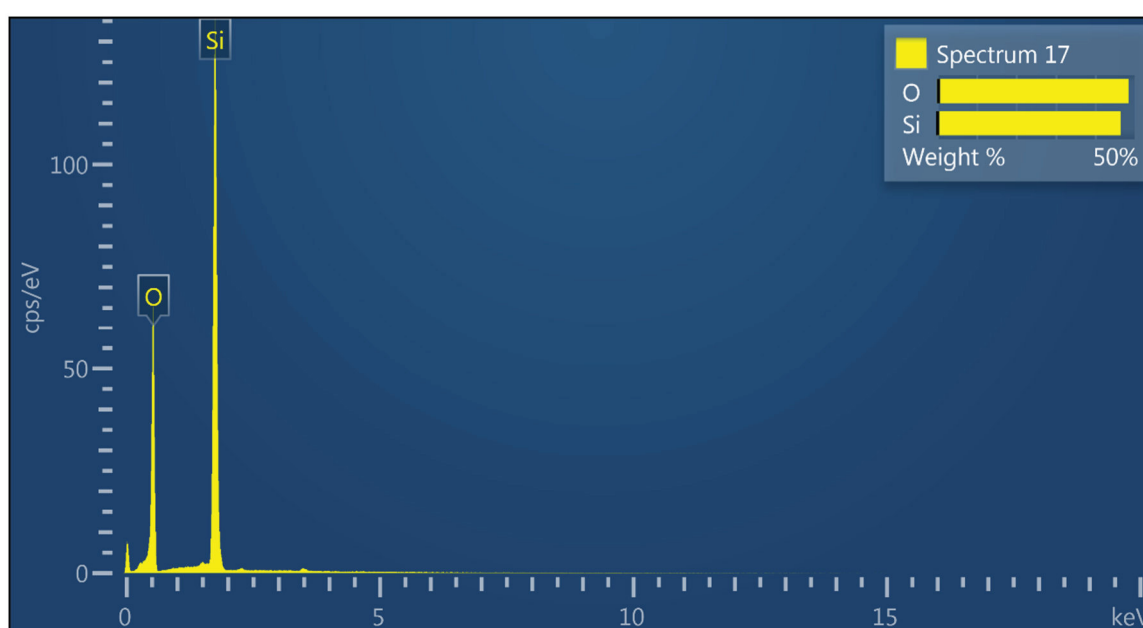


Figure 4.6. Example of an EDS spectrum.

Electron microprobe analysis (EMPA)

The electron microprobe analysis is a complementary technique to petrography used to determine the chemical composition of small selected areas examined within the samples. The EMPA is designed mainly for analysis but it can have an image function similar to SEM (Reed, 2005).

It consists essentially of an electron column and one or more X-ray spectrometers, which can be wavelength-dispersive spectrometers (WDS) and/or energy dispersive spectrometers (EDS) (Figure 4.7).

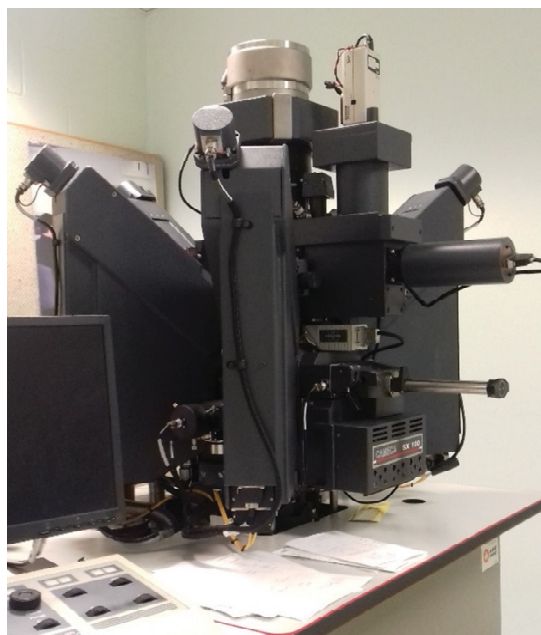


Figure 4.7. Electron microprobe instrument (Laval University).

The data are usually presented in the form of tables of weight percentages as oxides. According to Reed (2005), EMPA provides compositional information that assists in mineral identification.

Chemical analysis of the whole-rock composition

The whole-rock chemical analysis, also known as geochemical analysis, is a very important method because together with the petrographic analysis it provides complementary information about the rock composition.

Regarding the sample preparation for geochemical analysis, for example in the Actlabs Laboratories, located in Canada, about 30 g of each sample is needed for the analysis. The samples are first ground to powder. They are then fused and digested in a weak nitric acid solution and analyzed by the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The results allow to determine most elements at trace (parts per million), minor (percent), and major (percent) concentrations in the samples analyzed.

The data from the geochemical analysis are used to classify rocks through:

- a TAS diagram
- to calculate the norm of a rock.

TAS stands for *total alkali-silica* diagram and it is one of the most widely used classifications for volcanic rock. The sum of Na₂O and K₂O contents and SiO₂ content are taken from the oxides (wt%) of the chemical analysis and plotted into this diagram.

Le Maitre et al., (2002) indicate that to use the classification correctly, the chemical analyses must be recalculated to 100% excluding water and carbon dioxide; also, if a (Cross, Iddings, Pirsson and Washington) CIPW norm has to be calculated to determine the correct root name, the calculation of FeO and Fe₂O₃ should follow some procedures. Also, in TAS, basalt can be divided into alkaline or subalkaline/tholeiitic basalt (Le Bas et al., 1986). There are some differences between these two types of basalts regarding (Table 4.5): (1) the occurrence, (2) chemical composition and (3) petrography.

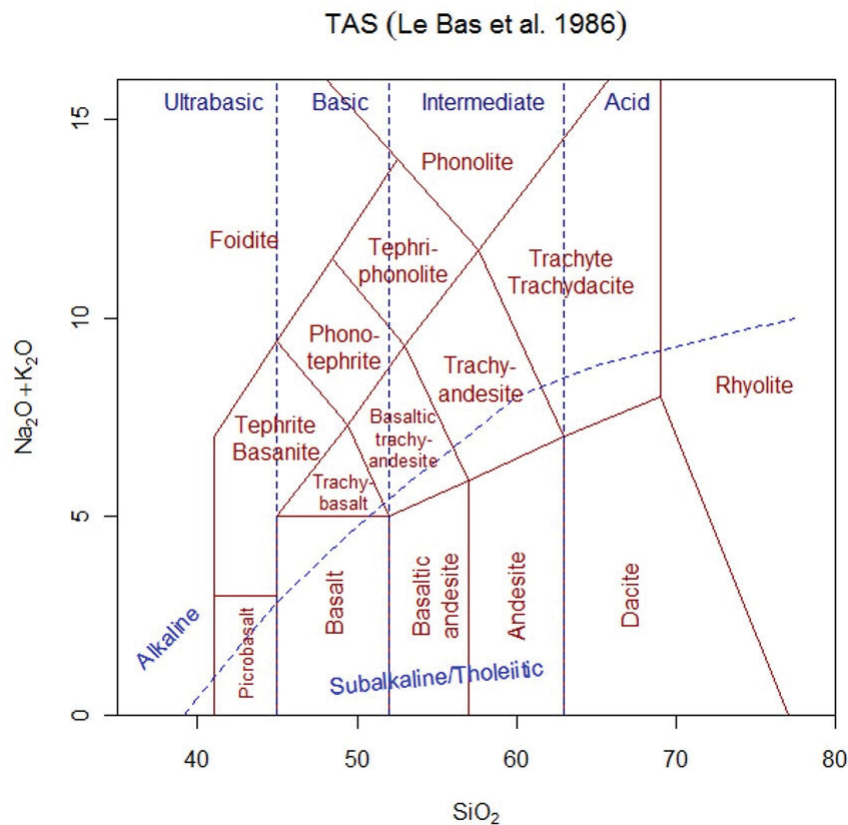


Figure 4.8. TAS diagram (Le Bas et al., 1986).

In TAS, some rock names need further criteria to separate them. This is the case between tephrite (ol <10 %) and basanite (ol >10 %) and also between trachyte (q <20 %) and trachydacite (q >20 %) (Le Bas et al., 1986; Le Maitre et al., 2002). The norm for both cases need to be calculated (ol = normative olivine; q = normative $100 * Q / (Q + or + ab + an)$) (Le Maitre et al., 2002). There are also three fields (trachybasalt, basaltic trachyandesite and

trachyandesite) that can be further subdivided depending on the relative amounts of Na₂O and K₂O (Le Bas et al., 1986; Le Maitre et al., 2002) (Table 4.6).

The Norm was initially created by three petrologists (Cross, Iddings, and Pirsson) and a geochemist (Washington), at the beginning of the twentieth century and became known as norm CIPW. Since then, several variations and alternatives were proposed (Rollinson, 1993; Winter, 2001) but the calculation became extremely popular (Le Maitre et al., 2002). It is a method that re-calculates the chemical analysis of an igneous rock into a set of ideal minerals (Winter, 2001) – normative minerals. A norm determines the virtual mineralogical composition of rock through chemical analysis. The CIPW norm calculation has to follow a set of rules and is usually calculated on a computer by using one of the several software (Fortran, NORRRM, GCDkit) available on the market. In the end, the normative minerals are expressed in weight percentages (wt%).

Table 4.5. Tholeiitic Basalts vs Alkali basalts

		Tholeiitic Basalts	Alkali basalts
Occurrence (Schmincke, 2004)		Typical of the ocean crust, flood basalts, some island arcs and in the volcanic islands of Iceland and Hawaii	In small volcanoes, on continents, on many oceanic islands
Elements (Schmincke, 2004)		Poor in K, P, Ti, Rb, Zr, Nb, U, Th	Enriched in K and Na Low concentration in SiO ₂
Petrography (Mackenzie et al., 1982; Le Maitre et al., 2002, Greenough et al. 2005)	Phenocrysts	- Olivine in small amounts or absent, generally unzoned - Plagioclase (Labradorite) - Augite and low-Ca pyroxene (pigeonite, hypersthene), generally pale-brown and zoning is not as apparent as in alkali basalt	- Olivine occurs in most samples, zoned with Fe-rich rims - Titanium augite, more strongly pleochroic with purplish–brown Ti-rich rims - Plagioclase less common than in tholeiites
	Groundmass	- Olivine is never present on the groundmass - Varying amounts of interstitial volcanic glass (brown) or devitrified volcanic glass - Granophyric intergrowths of quartz and alkali feldspar - Biotite absent - Quartz may be present in the matrix	- Olivine - Interstitial nepheline or analcite may be present - Biotite may be present in the matrix - Interstitial alkali feldspar is present but difficult to identify - Quartz absent
	Texture	Intergranular texture ophitic to subophitic texture Intersertal texture	Intergranular texture subophitic texture
Normative minerals (Yoder and Tilley, 1962)		Normative quartz, hypersthene and olivine. No nepheline	Normative nepheline and hypersthene.

The CIPW norm calculation can be used to know the degree of silica saturation for a variety of rocks. Based on the principle of the basalt tetrahedron (Yoder and Tilley, 1962), basalts can be classified according to the degree of silica saturation: (1) silica oversaturated – normative quartz and hypersthene in the norm; (2) silica saturated – normative hypersthene and (3) undersaturated – normative olivine and nepheline and no quartz.

Table 4.6. Further subdivisions of the TAS diagram.

Further subdivisions	Trachybasalt	Basaltic trachyandesite	trachyandesite
$\text{Na}_2\text{O}-2.0 \geq \text{K}_2\text{O}$	Hawaiite	Mugearite	Benmoreite
$\text{Na}_2\text{O}-2.0 < \text{K}_2\text{O}$	Potassic trachybasalt	Shoshonite	Latite

4.2.2. Mortar

Accelerated mortar-bar test at 80°C (AMBT)

The accelerated mortar bar test (AMBT) was originally developed at the National Building Research Institute (NBRI), in South Africa (Oberholster and Davis, 1986). It is one of the most widely used accelerated methods for evaluating the ASR of concrete aggregates (Fournier et al., 2006) as it only takes two weeks to have results regarding the expansion.

According to RILEM AAR-0 (2016), the AMBT is the second step to be used, after the petrographic examination, in assessing the ASR in aggregates.

The AMBT has been adopted in several countries in the form of standards, specifications and recommendations. Some of them are: ASTM C1260 (2014), CSA A23.2-25A (2019), and RILEM AAR-2 (2016). However, this method has shown to be unable to detect several aggregates that were considered reactive in the field (Hooton and Rogers, 1993; Fernandes et al., 2004, 2007; Hooton and Golmakani, 2016; Fernandes et al., 2017). This is the case for slowly reactive aggregates, such as granite, gneiss, quartzite (Fernandes et al., 2004; Castro et al., 2009; Castro, 2012), quartz gravel (Shayan and Freitag, 2017) and reactive carbonate aggregates susceptible to ACR (Fournier and Bérubé, 2000). The AMBT identifies aggregates as reactive that are not necessarily reactive in the CPT or the field. Therefore, it is recommended that the AMBT is not used for rejecting aggregates (Fournier and Bérubé, 2000; Fournier et al., 2006) or as the only method to assess ASR (Hooton and Golmakani, 2016).

On the contrary, a good experience with this method has been reported in the inter-laboratory trials by RILEM (Nixon and Sims, 2000) and by the EU “PARTNER” project (Lindgård et al., 2010). Both experiences with this test method have shown that there is a good

correlation between laboratory tests and field performance, being considered one of the most effective RILEM methods.

A SWOT analysis is made for the AMBT method showing the strengths and limitations of this method (Figure 4.9).

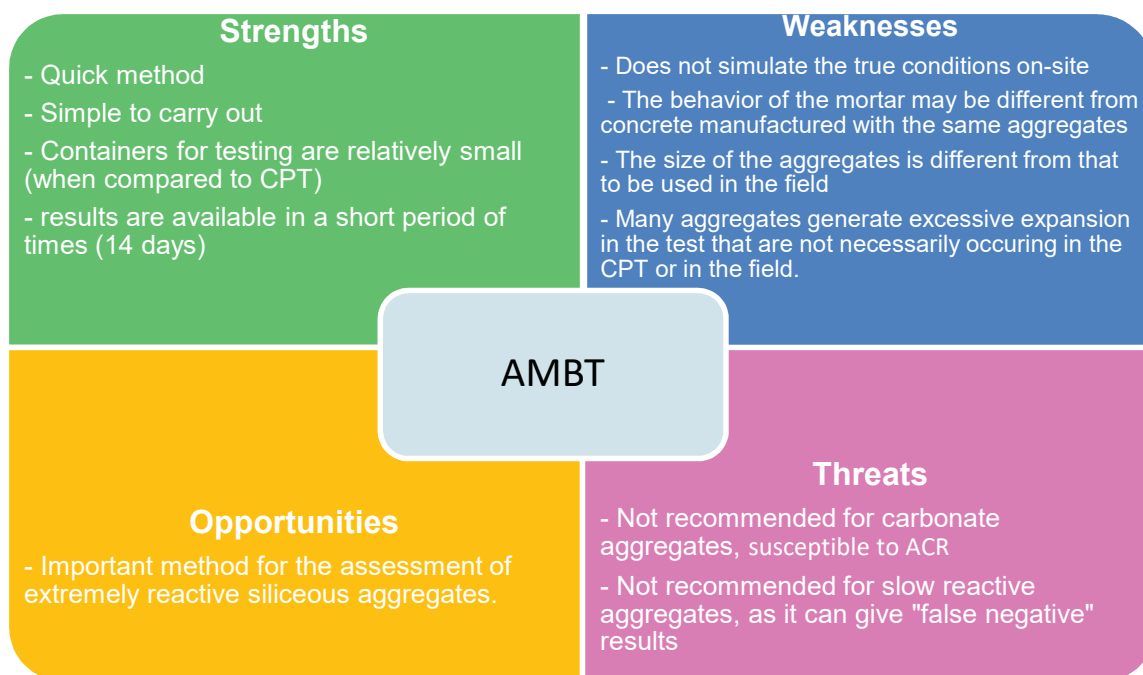


Figure 4.9. SWOT analysis of AMBT method.

Table 4.7 shows a comparison of the parameters used among different accelerated mortar bar test methods according to ASTM C1260 (2014), CSA A23.2-25A (2019), and RILEM AAR-2 (2016). The main differences are the values of the expansion thresholds, the alkali content in cement, the aggregate grading size and the w/c ratio.

In general terms, the procedure follows the following steps:

- 1) three mortar bars with a specific size are prepared using natural or crushed to standard sizes aggregates and mixture proportions;
- 2) they are cast into mortar bar moulds;
- 3) the mortars are in moist curing in their moulds for 24h;
- 4) After demolding, the bars are submerged in water and heated to 80°C for 24h;
- 5) Their first length measurement is recorded;
- 6) The bars are transferred to a solution of 1 N of NaOH at 80°C for 14 days;
- 7) Measurements are made periodically during the 14 days (Figure 4.10);

8) If necessary, the test period can be extended to 28 days.

Table 4.7. Comparison of different accelerated mortar bar test methods according to ASTM C1260 (2014), CSA A23.2-25A (2019), and RILEM AAR-2 (2016).

	ASTM C1260 (2014)	CSA A23.2-25A (2019)	RILEM AAR-2 (2016)
Expansion Limits	< 0.10% non-reactive > 0.20% potentially deleterious 0.10-0.20% aggregates known to be innocuous and deleterious in field performance (ASTM C 1778, 2020)	< 0.15 % non-reactive ≥ 0.15% - ≤0.44% highly reactive ≥ 0.44% extremely reactive (CSA 23.2-27A)	< 0.10% non-reactive > 0.20% potentially deleterious 0.10-0.20% regarded as being potentially alkali-reactive.
Duration	14 days	14 days	14 days
Specimens dimensions	25 x 25 x 285 mm (ASTM C490/C490M)	25 x 25 x 285 mm	25 x 25 x 285 mm (AAR-2.1) 40 x 40 x 160 mm (AAR-2.2)
Alkali content of cement	negligible or minor effects on expansion	0.90 ± 0.10%	Min. 1.0%
Aggregates grading size	> 150 µm and < 4,75 mm	≥ 160 µm and ≤ 5 mm	≥ 125 µm and ≤ 4 mm
w/c	0.47 by mass	0.44 by mass (Natural fine aggregates) 0.50 by mass (crushed coarse aggregates or manufactured sands)	0.47 by mass
Storage conditions	1 N NaOH at 80 ±2.0°C	1 N NaOH at 80 ±2.0°C	1 M NaOH at 80 ±2.0°C



Figure 4.10. Measuring the mortar bar of the AMBT method.

4.2.3. Concrete

Concrete prism test at 38°C (CPT)

The Concrete Prism Test is one of the most reliable tests to assess ASR potential in concrete aggregates. It is considered the test that best simulates the conditions of the field concrete. CPT is the last of the three stages for assessing potential AAR recommended by RILEM AAR-0 (2016), and it is a long-term test using concrete specimens.

The method aims at evaluating the potential alkali-reactivity of coarse or fine aggregates, or a combination of fine and coarse aggregates (CSA 23.2.14A, 2015). Also, in RILEM AAR-3 (2016), the test method is applied to aggregate combinations. In the CSA concrete prism test (23.2.14A, 2015), concrete mixed with a well-known reactive coarse aggregate, named Spratt and non-reactive sand is used as a reference to confirm the reliability of the testing conditions.

Recommendation RILEM AAR-0 (2016) states that the test is suitable for all aggregates except for those identified as “slowly” reactive aggregates. For those cases, the period of the test should be extended to 2 years. Also, the recommendation RILEM AAR-3 (2016) indicates that the test method has been developed for normal weight aggregates but is not necessarily applicable for lightweight (particle density < 2000 kg/m³) or heavy weight aggregates (particle density > 3500 kg/m³).

The test is performed under high humidity conditions with prisms stored at a temperature of 38°C over water in sealed plastic containers with wicks. In a previous version of RILEM AAR-3 (RILEM AAR-3, 2000), the storage conditions implied that the prisms were wrapped with a humid cloth instead of a wick placed around the wall of the container described in the most recent version of the RILEM AAR-3 (2016). The practice of using wrapping specimens is not consensual although it has been used for research purposes (Kawabata et al., 2016; Lindgård et al. 2010; Yamada et al., 2016). The wrapping specimens have been used to avoid alkali leaching of the concrete specimens (Kawabata et al., 2016; Yamada et al., 2016). Moreover, it has been found that the wrapping of specimens produces higher expansions when compared to unwrapped specimens (RILEM AAR-3, 2000; Yamada et al., 2016).

Alkali leaching is defined as the loss of alkalis in the concrete prism during curing (Rivard et al., 2003; Lindgård et al. 2013). It has been reported as one of the problems with the concrete prism tests as the storage conditions of CPT appear to allow leaching of a large proportion of the alkali initially present inside the specimens (Bérubé and Fournier, 1993a). It seems that the removal of the wicks from the storage containers contributes to the reduction of the expansion (Swamy, 1992) but Bérubé and Fournier (1993a) emphasize that high humidity is

more critical for these tests than alkali leaching. Also, Yamada et al. (2014) highlight that alkali leaching seems to be limited at 40 °C and only significant at 60 °C.

The main disadvantage of CPT is related to the duration of the test which takes one year to perform. Another disadvantage of the use of this method is described by Grattan-Bellew and Katayama (2017) and is related to the use of a specific mixture design of concrete. The authors question how to predict the field performance: (1) of mixtures with lower cement contents and (2) of mixtures with lower alkali cement. It is important to highlight that the results from the EU-PARTNER project for the RILEM AAR-3 CPT method showed that the repeatability is good, whereas the reproducibility is quite poor among laboratories.

A SWOT analysis is presented in (Figure 4.11).

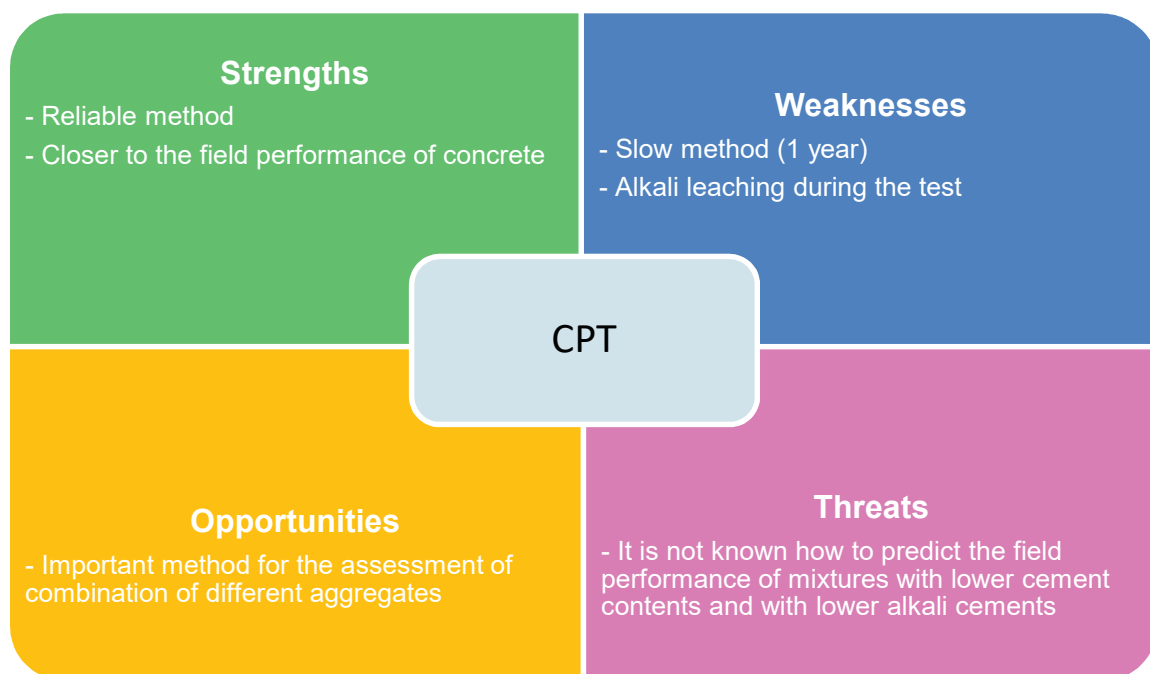


Figure 4.11. SWOT analysis of CPT method.

A comparison was made between the ASTM and CSA standards and the recommendation of RILEM AAR-3 (2016) for the CPT method (Table 4.8). The main difference is related to the value of alkali content of cement, which is higher for RILEM AAR-3 (2016), and therefore this is the least conservative standard.

Generally, the procedure develops in the following steps:

- 1) three concrete prisms, with a standardized dimension, are prepared with specific coarse and fine aggregates using specified mixture characteristics;
- 2) they are cast into prism moulds and kept there for 24h;

- 3) After demolding the first length measurement is recorded (Figure 4.12);
- 4) Then, they are stored above water in a sealed plastic container/pails (with a wick placed around the wall of the container) and placed in a chamber at 38°C for one year (Figure 4.13A and B);
- 5) Measurements are done periodically for up to one year;
- 6) If necessary, the period of time can be prolonged to two years, especially for evaluating the effectiveness of SCMs to prevent expansion due to ASR.

Table 4.8. Comparison of different concrete prism test methods according to ASTM C1293 (2020), CSA A23.2-14A (2019), and RILEM AAR-3 (2016).

	ASTM C1293 (2020)	CSA A23.2-14A (2015)	RILEM AAR-3 (2016)
Expansion Limits	< 0.04 % non-reactive ≥0.04% - <0.12% moderately reactive ≥0.12%-<0.24% highly reactive ≥0.24% very highly reactive (ASTM C 1778, 2020)	< 0.040 % non-reactive ≥0.040%-<0.120% moderately reactive ≥0.120%-<0.260% extremely reactive ≥0.260% extremely reactive (CSA 23.2-27A)	< 0.05 non-reactive > 0.10% reactive 0.05-0.10% regarded as being potentially alkali-reactive. (RILEM AAR-0, 2016)
Duration	12 months	12 months	12 months
Specimens dimensions	75 x 75 x 250 mm (ASTM C490/C490M)	> 75 x 75 x 275 mm < 75 x 75 x 405 mm	75 x 75 x 250 mm 75±5 mm 250±50 mm
Alkali content of cement	0.9 ±0.1%	0.90 ±0.10%	1.25 ±0.05%
Aggregates grading size	> 4.75 mm and < 19.0	>5 mm and < 20 mm	≥ 0.125 mm and ≤ 22.4 mm
w/c	0.42 to 0.45 by mass	0.42 to 0.45	
Coarse to fine aggregate ratio		60:40	60:40
Storage conditions	Stored under high relative humidity conditions at 38°C	Stored under moist conditions at 38°C	Stored under high humidity conditions at 38°C

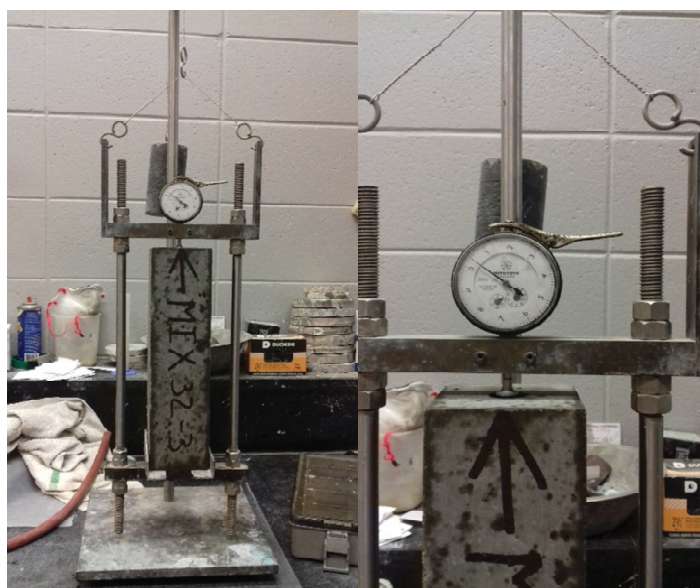


Figure 4.12. Measurement of a prism for the CPT method.



Figure 4.13. Plastic container /pails: A) with a wick and 3 prisms inside a rack; B) inside a chamber at 38°C.

Gel Pat Test

The Gel Pat Test (GPT) is a method that consists in determining the susceptibility of an aggregate within the concrete to form a siliceous gel in the presence of a high alkaline solution. It allows for the identification of the reactive particles of different types of aggregates.

The method was first described by Stanton and co-authors in the 1940s (Bredsdorff et al., 1960; Bérubé and Fournier, 1993) and later by Jones and Tarleton (1958). The procedure

from the last two authors has been adapted in the form of an appendix of the British Standard – BS 7943 - as a method for the detection of opal (or other similarly highly reactive silica) in aggregates (Poole and Sims, 2016). However, Sims and Nixon (2003b) say that slower reactive materials are not detected by this method.

Fournier and Bérubé (1993b) described the application of a modified GPT to determine the potential alkali-silica reactivity of carbonate aggregates. In this test method, the authors immersed polished concrete slices (specimens cast at the same time as prisms made for the CPT, then cut and polished slightly to remove surface roughness due to cutting with the diamond saw) into 1N NaOH solution at 38°C for 56 days, during which they were examined and photographed at regular intervals. To quantify the amount of gel formed on the polished concrete sections, the authors developed a rating system called the Gel Pat Test Rating (GPT_r) where they used: (1) the proportion of particles showing gel deposits on their surface and (2) the average amount of gel formed at the surface of the particles. They also proposed the Gel Rating (Gr). In the GPT_r procedure, the aggregate particles are identified on the gel-free plate (T₀) and then examined in the photograph at time T = 56 days and classified according to four categories: (A) particles without gel, (B) particles with traces of gel, (C) particles with a significant amount of gel and (D) particles with an abundant amount of gel. The Gr is calculated by multiplying the number of particles in each category with gel by a specific multiplication factor to each category, and then adding these numbers and dividing them by the number of particles with gel. The GPT_r is obtained with the total number of particles on the sample.

Villeneuve (2011) used this method in her research and concluded that it is an effective tool for the identification of certain reactive facies in different aggregates, but depends on the type of aggregate. The GPT correlated better with DRI than with the expansion tests. The same author also states that the quantification of gel was based on a visual estimation, which is not the best way to quantify. However, the author recognized a tendency between the aggregate particles that reacted similarly during the GPT test. She recognized different categories of reaction product formation according to the types of aggregates giving a better correlation with the expansion of the CPT.

More recently, Lanza and Alaejos (2012) proposed an optimized GPT based on the one described in BS 7943. The authors raised the storage temperature to 80°C of disc specimens immersed in a NaOH solution and shortened the test exposure from 14 days to 3 days. They also made a cement-aggregate mixture with abundant voids among the particles to facilitate the accumulation of gel inside the voids. They concluded that with this GPT version, it was possible to detect not only opaline silica but cryptocrystalline or microcrystalline quartz and

other reactive components that were not possible to identify by the GPT described in the original version in the British Standard.

GPT was recommended as a useful rapid test for reactive material and was possibly used more in the UK than elsewhere (Sims, 2017). Canada has also been using this method in some works by Fournier and Bérubé (1993b), Tremblay et al., (2012) and Villeneuve (2011). In Spain, Lanza and Alaejos (2012) have reported the use of a modified Gel Pat Test in their research. The Czech Republic has also used this method as one of the methods to determine the reactivity of aggregates (Fernandes et al., 2017). But, in general, this method seems to be practiced in just a few countries.

A SWOT analysis was done to know mostly the strengths and limitations of the GPT method (Figure 4.14).

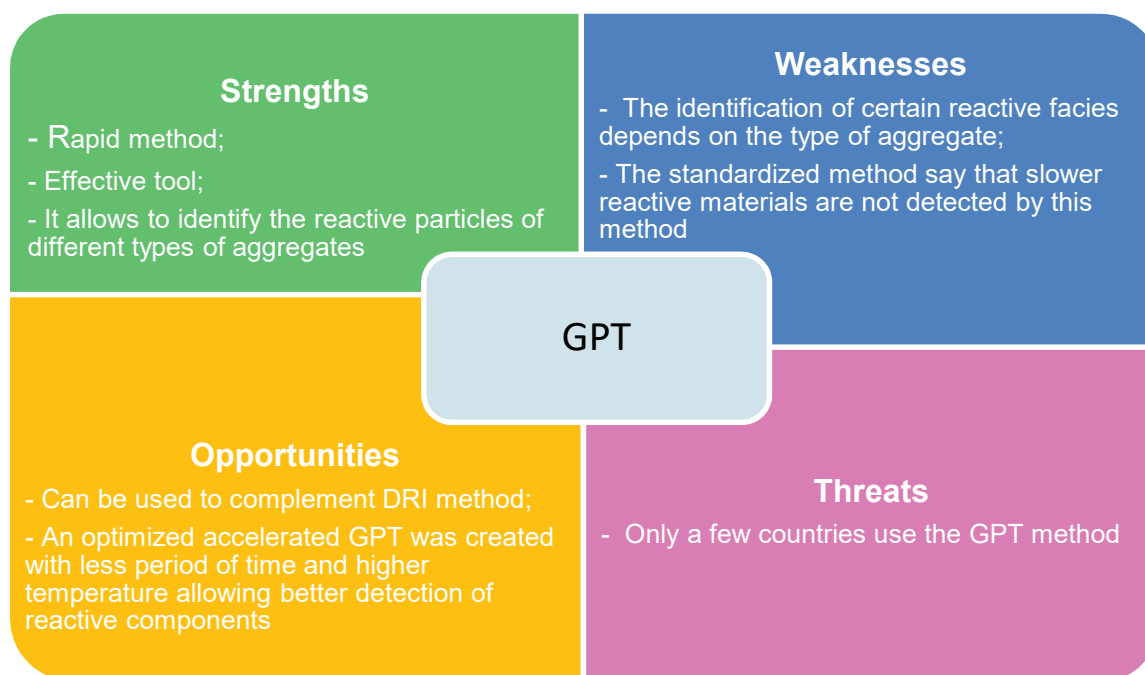


Figure 4.14. SWOT analysis of GPT method.

In this study, the procedure done for this method followed the next steps:

1. Concrete cylinders or prisms were cast with the same mix as for CPT;
2. After 24h, the cylinders/prisms are removed from the moulds and placed in a moisture room for a week at 38°C;
3. The cylinders/prisms are then cut in half lengthwise, and one of the sides is slightly polished to remove surface artefacts due to the cutting operation;

4. The samples were then placed in a 1N NaOH solution at 38°C. the samples were stored in the solution for a total of 19 weeks and examined / photographed at regular intervals during that period (Figure 4.15);
5. The opposite side of the cylinders/prisms is usually used for petrographic examination (e.g. DRI method), or to examine (e.g. thin sections) the particles that have reacted and produce gel deposits at their surface (Figure 4.15).

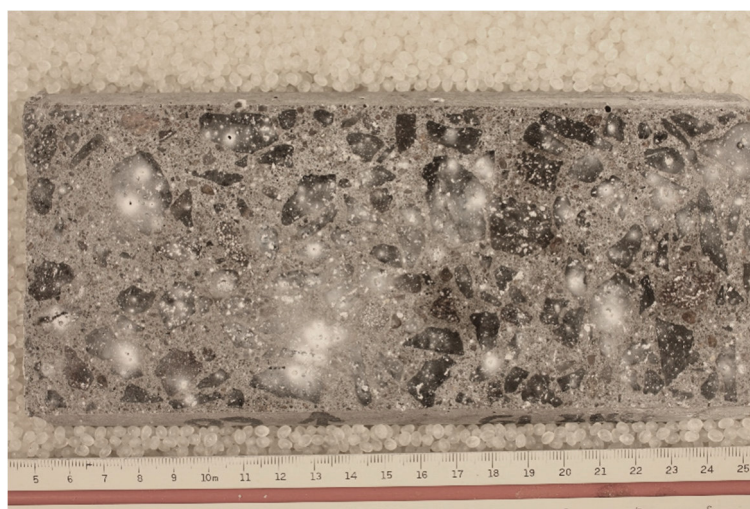


Figure 4.15. Example of a concrete prism subjected to the GPT method.

Petrographic examination

Damage Rating Index (DRI)

The DRI is a semi-quantitative petrographic method used to evaluate damage in concrete due to ASR. Despite being originally developed for concrete affected by ASR, it can also be used for other forms of deterioration like ACR, cycles of freezing and thawing, external/internal sulfate attack and delayed ettringite formation (Grattan-Bellew and Mitchell, 2006). This method can be used in concrete cores from damaged structures and for concrete manufactured in a laboratory.

The method was initially developed, in the 1990s, by P. E. Grattan-Bellew from the National Research Council of Canada to evaluate concrete damaged by ASR (Rivard et al., 2002; Villeneuve, 2011). Several authors have tried different methods to quantify the deterioration caused by ASR (Blight et al., 1981; Sims et al., 1992; Broekmans, 2002) but the DRI from Grattan-Bellew was the one that had more international recognition (Poole and Sims, 2016). More recently, a modified DRI method was proposed by Villeneuve (2011) and has been

implemented especially in Canada. This version is based on the original and revised DRI method by P.E. Grattan-Bellew (Villeneuve, 2011; Villeneuve et al., 2012; Fecteau et al., 2016). The major difference between the methods is related to the values of the weighting factors of each feature that are quantified in the test specimens (Villeneuve et al., 2012; Fournier et al., 2015).

The DRI method uses a stereomicroscope (~15x magnification) to observe and count different typical features within a 1 cm² grid drawn on the surface of a polished concrete section.

A petrographic album was prepared, at Université Laval in 2015, to assist petrographers in the DRI method. The main objective is to reduce variability among petrographers/operators carrying out the DRI. The album describes and illustrates the different petrographic features of deterioration in polished concrete sections of aggregate particles size larger than 2 mm (Fournier et al., 2015).

Table 9 shows the different features to identify and the weighing factors of each feature proposed by Villeneuve (2011) and Villeneuve et al., (2012).

Table 4.9. Petrographic features and weighing factors are used in the determination of DRI (Villeneuve, 2011; Villeneuve et al., 2012; Fournier et al., 2015).

Petrographic features		Weighting features
Cracks in the aggregate particle	Closed (without reaction products)	0.25
	Opened or in a fine network (without reaction products)	2
	Opened or in a fine network (with reaction products)	2
Cracks in the cement paste	without reaction products	3
	with reaction products	3
Debonded aggregate		3
Reacted aggregate particle		2
Reaction rim		-
Reaction products in voids of the cement paste		-

In this study, the procedure was performed as follows (Villeneuve, 2011; Villeneuve et al., 2012; Allard et al., 2016):

1. A concrete specimen is cut in half and one of the surfaces is finely polished;
2. A grid of 1 cm² is drawn in a minimum size concrete polished surface of 150 cm² (Figure 4.16)

3. Each square is examined under a stereomicroscope ($\sim 15\times$ magnification) for petrographic features of ASR (e.g. cracks in the aggregate particles, cracks in the cement paste, debonded aggregates, as presented in Table 4.9);
4. All of the values counted per each square are inserted in an excel sheet already prepared for the DRI forming a DRI damage map (Figure 4.17).
5. The sum of each feature is counted and multiplied by the respective weighting factor;
6. The total sum is normalized for a surface area of 100 cm^2 , which provides the DRI value for the test specimen.

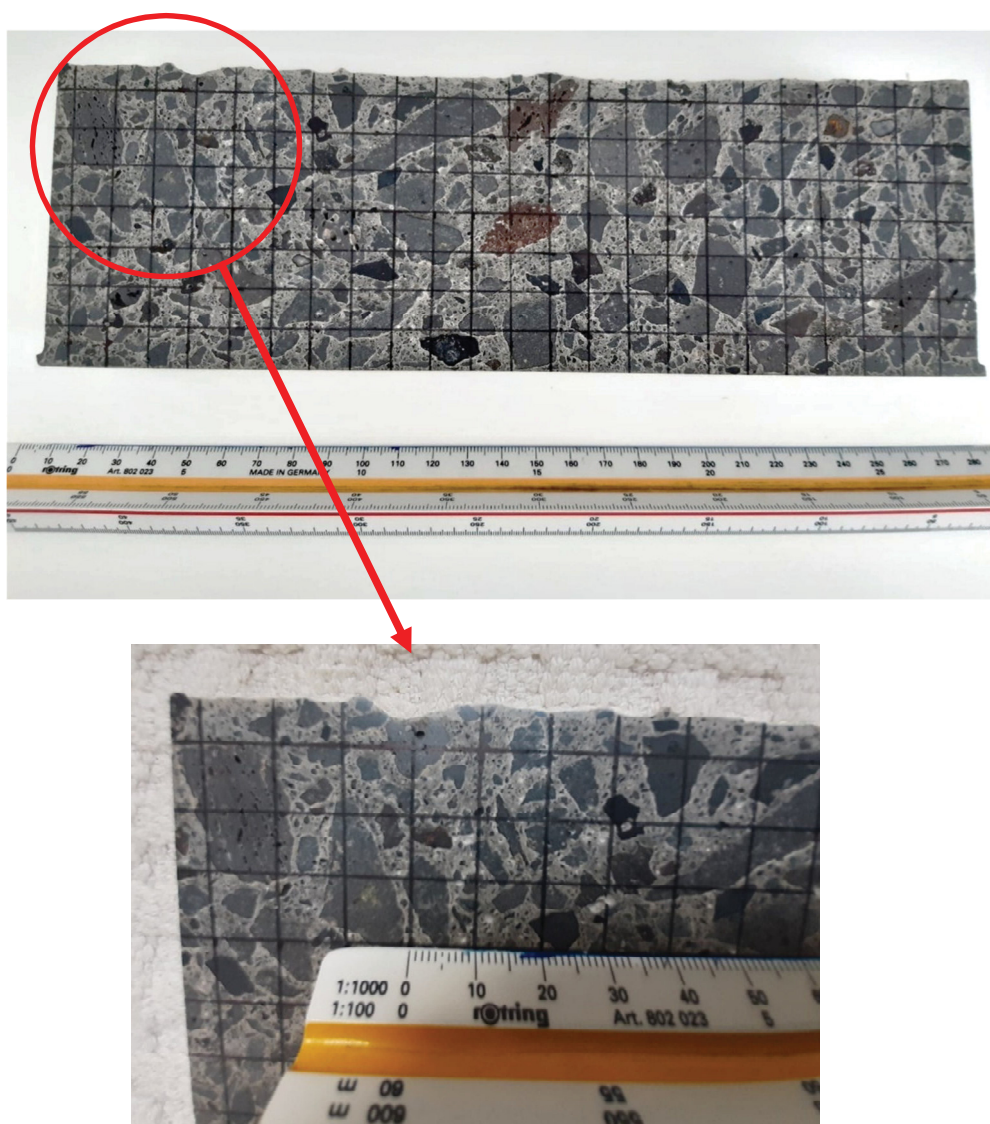


Figure 4.16. Concrete polished surface with a drawn grid of 1 cm^2 .

Shrimer (2015) reports that DRI has been used to assess the degree of deterioration in concrete due to ASR, but also to compare the relative degree of damage between various components of the structure. DRI is a simple method that gives important information regarding the type and the extent of deterioration in the concrete under evaluation.

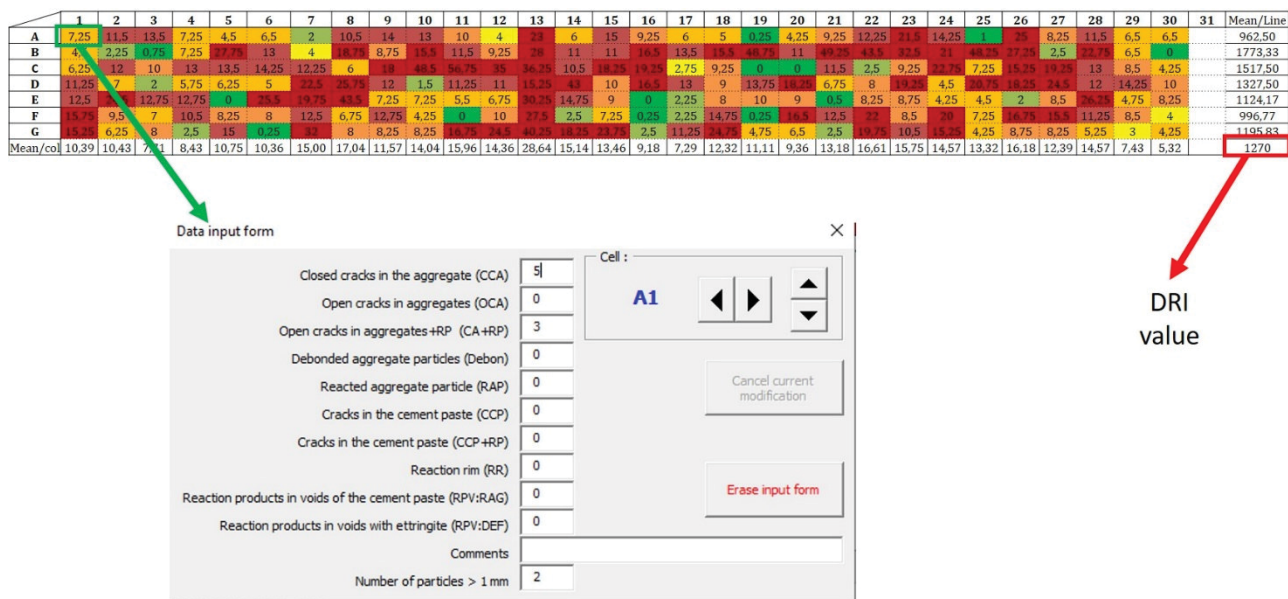


Figure 4.17. Example of a DRI damage map in an excel sheet.

The reliability of the modified DRI method (Villeneuve, 2011; Villeneuve et al., 2012) was assessed by Sanchez et al., (2015) and a DRI damage classification was proposed by Fournier et al., (2015). Sanchez et al., (2015) showed that increasing DRI numbers are generally correlating with increasing expansion due to ASR. Also, Shrimer (2015) found a good correlation between a visual damage rating of two dams in the field and DRI values obtained from cores extracted from both structures. Powers and Shrimer (2007) verified that the DRI method produced good results in several investigations of different structures. Sanchez et al., (2015) concluded that the DRI value can provide a reliable assessment of the degree of expansion in concrete samples incorporating reactive fine or coarse aggregates.

The DRI damage classification shows different ranges of DRI values. It is based on petrographic observations of concrete cores extracted from piers of a concrete bridge with signs of deterioration by ASR in Eastern Canada (Fournier et al., 2009). Table 4.10 shows the information presented in Fournier et al., (2015) on the different ranges of DRI values associated with the typical petrographic features of deterioration.

Table 4.10. Different ranges of DRI values are associated with the typical petrographic features of deterioration (Villeneuve, 2011; Villeneuve et al., 2012; Fournier et al., 2015)

DRI	Degree of ASR
< 200/250	Trace Concrete is in good condition
	▪ <i>Macroscopic level</i>: no significant signs of deterioration are visible. ▪ <i>Microscopic level (stereomicroscope)</i>: mainly closed cracks within the coarse aggregate particles, sometimes filled with ASR gel that is rarely extending into the cement paste. Some reaction rims surround coarse aggregates. Cement paste with noticeable to mild cracking (< 0.02 mm in width). Voids in the cement paste have limited deposits of secondary products being the majority of the cases ettringite.
200/250 - 400	Fair to moderate Concrete is generally in good condition
	▪ <i>Macroscopic level</i>: fair signs of deterioration are visible. ▪ <i>Microscopic level (stereomicroscope)</i>: mainly fine cracks in several aggregate particles, with part of them filled with ASR gel. Aggregate cracks rarely extend into the cement paste. Significant reaction rims surrounding aggregate particles. Cement paste with mild to significant cracking (< 0.02 mm to 0.05 in width). ASR gel is visible in some of those cracks. Voids in the cement paste with secondary products are present in a fair number of them. The majority of the cases correspond to ettringite.
400 – 700/750	Moderate to severe Concrete with moderate signs of deterioration
	▪ <i>Macroscopic level</i>: moderate signs of deterioration are visible. ▪ <i>Microscopic level (stereomicroscope)</i>: cracks are present in a big part of the aggregate particles, with a large significant of them filled with ASR gel. Aggregate cracks extend into the cement paste in most cases and sometimes connect with reactive particles. Significant to a large proportion of reaction rims surround aggregate particles. Cement paste with significant to important cracking (< 0.02 mm to 0.05). Several cracks with ASR gel. Voids in the cement paste with secondary products are present in a significant number of them with both ettringite and ASR gel.
>700/750	Severe to very severe Concrete with severe signs of deterioration
	▪ <i>Macroscopic level</i>: severe signs of deterioration are visible with cracking in aggregate particles and in the cement paste ▪ <i>Microscopic level (stereomicroscope)</i>: description similar to the range before. Cracks are found connecting reactive aggregate particles with one another.

This classification demonstrates that the higher the DRI number is the worse the degree of ASR of a sample of concrete studied.

Several researchers have been using the DRI but so far there is not a standard test procedure (Sanchez et al., 2015). Poole and Sims (2016) state that this is due to the variability of results among operators/petrographers from different laboratories. However, the same authors affirm that a single operator reproducibly is very good. The research of Villeneuve et al., (2012) revealed that the variability can be largely reduced by improving the definition of the different features of deterioration and by giving proper training to petrographers using

reference sections and well-illustrated instructions. Grattan-Bellew and Mitchell (2006) sustain that other variables can influence in this counting like the light source or the quality of the polished section, among others. Also, some variability happens when DRI is done by the same operator. Champagne (2020) made a statistical analysis to determine the variability attributed to the same operator and concluded that some variability is still present as a very high point coefficient of variation ranging from 61.0 to 120.4% has been obtained for an experienced operator. The same author states that the experience of the operator greatly influences the variability, while some experience is required to obtain reasonable consistency. It can be said that the DRI method has a subjective character mainly because it depends on the experience of the operator in counting the different petrographic features.

A SWOT analysis was done on the DRI method to identify its strengths, weaknesses, opportunities and threats (Figure 4.18).

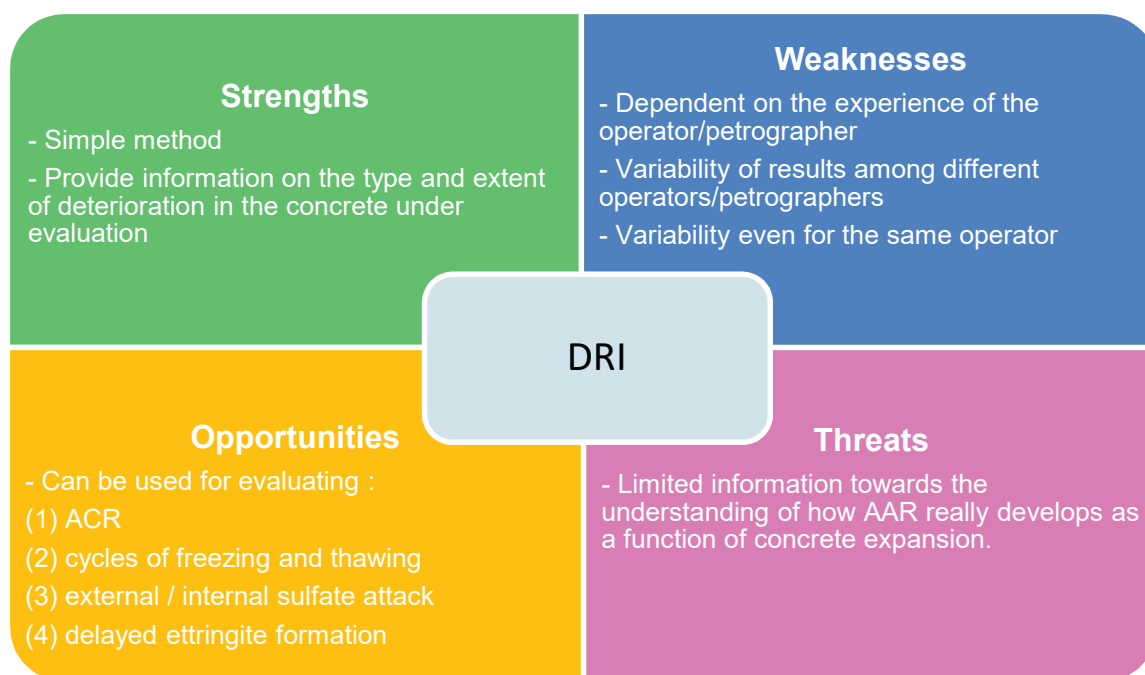


Figure 4.18. SWOT analysis of DRI method.

Overall, Powers and Shrimmer (2007) affirm that DRI can be easily understood by engineers, concrete specialists, and those who are responsible for the control and management of structures with ASR. Shrimmer (2015) interprets the DRI as qualitative/descriptive petrographic data transformed into a numeric value that can be easily understood.

Petrographic examination of mortar and hardened concrete

The approach is similar to the petrographic examination conducted on rock thin-sections. The difference between mortar and concrete is that the maximum particle size of the coarser aggregate of a mortar is normally below 4mm.

There are different binders used for mortars that can be examined under a microscope. Portland cement have been broadly used for building construction since the 1930s (Ingham, 2011). It is more impermeable and stronger when compared to other binders.

In the 1960s, thin sections of 30 μm in thickness became widely used for petrographic examination of concretes and mortars (Poole and Sims, 2016). The polarising microscope is the most important instrument used for the petrographic examination of concrete and related materials; it should be the first step used for the detailed examination of concrete (Poole and Sims, 2016)

Several features can be seen when using concrete thin sections under the polarizing microscope. Ingham (2001) indicates that the main applications for concrete petrographic are:

- Identifying the mix ingredients including coarse and fine aggregate, cement type, fillers, mineral additions, and certain additives;
- Determining the mix proportions and air void content;
- Assessing the quality of workmanship;
- Screening for evidence of distress or deterioration;
- Diagnosing the causes, severity, and extent of defects and deterioration.

For ASR it is important to identify: (1) microcracks, (2) the presence of gel, (3) which rock facies within the aggregates are reactive, (4) reaction rims and (5) cement paste-aggregate bond.

There is more detailed information that can be obtained from petrographic analysis of concrete, which is delivered in dedicated courses (e.g. PELCON, Danish Technological Institute). Some of this information helps to identify, among others:

- cement types;
- pozzolans;
- cracks;
- degree of hydration;
- carbonation,
- AAR, sulphate attack, frost damage, DEF, fire attack.

Furthermore, there are two important books in the literature about concrete examination entitled “Concrete Petrography”. These two books can be used by petrographers with complete information regarding concrete and its problems. The first edition was written by John, Poole and Sims (1998) and the second edition by Poole and Sims (2016). The second edition is a revised and updated version of the first one. The second edition provides detailed information regarding concrete and cementitious materials that includes: (1) petrographic equipment and methods, (2) sampling and specimen preparation, (3) composition of concrete, (4) appearance and textures of cementitious materials, (5) examination of deteriorated and damaged concrete, (6) precast and special concretes and (7) all types of cementitious materials.

From the point of view of ASR, the petrographic examination of concrete is quite important because it helps to identify the rock types of aggregate particles with the reaction that contains cracks and gel (Godart and De Rooij, 2017). Regarding the cracks, ASR is not the only phenomenon in concrete that causes expansion and/or internal cracking, also (BCA, 1993):

- plastic shrinkage;
- thermal contraction;
- drying shrinkage;
- aggregate expansion and contraction;
- sulfate attack;
- frost attack;
- steel corrosion.

The concrete examination is performed either in concrete from damaged structures or in concrete manufactured in a laboratory. Poole and Sims (2016) made a schematic diagram with five stages of the complexity of concrete petrographic investigation (Figure 4.19):

Stage 1: states that the scientific investigation will begin with an inspection of the structure and/or manufacturing process itself. For simple situations, this information is enough but for the majority of cases, more investigation is required and should be carried out at a laboratory.

Stage 2: if the additional information required is simple, physical tests and visual inspection by a competent petrographer can be done on rock types and their proportions present in an aggregate sample, in a concrete slab or a mortar, with the help of a hand lens and binocular microscope.

Stage 3: in this stage, definitive identification of some minerals and fine-grained materials, as well as particulate admixtures and fine-grained aggregates is required. For that, it is

necessary the use of a petrographic polarising microscope, and possibly a scanning electron microscope, X-ray diffractometer, or other specialized equipment.

Stage 4: in this stage, if quantitative information is required, it is necessary to use specialized equipment. There are plenty of methods available for quantitative or modal analysis, which can range from simple sieve analysis of an aggregate sample to various mechanical and automated modal analysis methods.

Stage 5: for more complex investigation, besides the visual and microscopic techniques, it is necessary to use more specialized equipment (SEM, EMPA, XRD, chemical analysis, etc).

Godart et al., (2013) indicate that an examination of the concrete thin sections should be performed to establish the cause of concrete damage. In this recommendation, petrographic examination allows for the identification of cement clinker phases in the concrete. This recommendation describes procedures and methodologies used especially to obtain a diagnosis of damaged concrete caused by ASR.

The ASTM C 856 (2020) is one of the few standards used for the petrographic examination of hardened concrete. In this standard, the samples that can be examined include those taken from concrete constructions, or it can be concrete or mortar specimens that have been exposed to natural environments or those that simulated service conditions or subjected to laboratory tests. It can be applied to all types of hardened mixtures, such as: concrete, mortar, grout, plaster, stucco and terrazzo. The petrographers must have the same requirements as those described in the petrographic examination of concrete aggregates (ASTM C 295/295M, 2019). The petrographic examination is very similar to the schematic diagram illustrated by Poole and Sims (2016). The concrete petrographic procedure begins with a visual examination of each sample, which is then followed by an examination using a stereomicroscope. For more detailed information, petrographic or metallographic microscopes are used, SEM, or XRD and chemical or physical tests can be applied (ASTM C 856, 2020). Several information can be obtained when using a petrographic microscope in a concrete thin section such as: (1) characteristics of coarse and fine aggregates, (2) relict cement grains and hydration products and characteristics of cement paste (Table 4.11 and 4.12).

In conclusion, petrographic examination of concrete is one of the methods accepted to confirm the presence of ASR, it is usually done by the study of thin sections under an optical microscope and sometimes is complemented by other methods such as SEM/EDS and geochemical analysis (Godart and De Rooij, 2017).

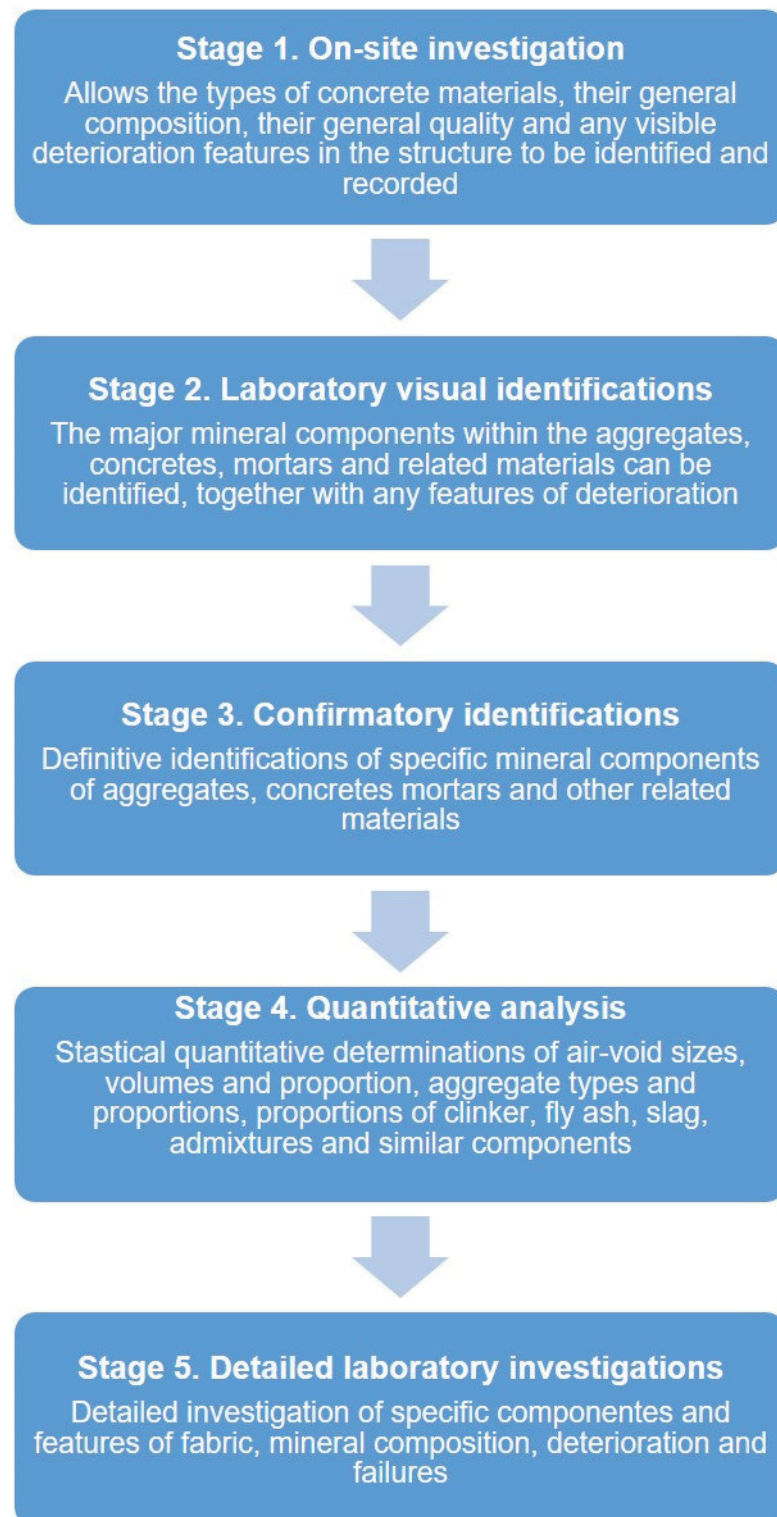


Figure 4.19. Schematic diagram with different stages of the complexity of petrographic investigation (Poole and Sims, 2016).

Table 4.11. Petrographic examination of concrete thin sections (ASTM C 856, 2020)

Fine and coarse aggregates	Relict cement grains and hydration products	Characteristics of cement paste
- Mineralogy, texture, fabric - Grading, grain size and nature of internal boundaries in aggregate, classification of coarse and fine aggregate. - Natural mineral aggregate or crushed stone; natural or manufactured fine aggregate - Bond with matrix; peripheral cracks inside the borders of aggregate grains; internal cracks. General microfractures if one can establish that they existed before thin-sectioning. - Alkali – carbonate reactions - Alkali – silica reaction (see Table 4.12)	- In concrete over two years' old and normally cured, the only residual cement grains are those that were largest, which may be composed of several constituents or be of alite or belite (substituted C3S and C2S). The latter two may be bordered by one or two layers of gel having different indexes of refraction, or by a layer of calcium hydroxide. The largest relict grains may be truly unhydrated and retain the low (dark grey) birefringence of alite in distorted quasihexagonal sections and the visible birefringence to the first-order yellow of the lamellar twins in rounded grains of belite. Interstitial aluminoferrite appears as prismatic grains ranging in color from brown to greenish brown to reddish brown and having a high refractive index and pleochroism masked by the colour of the grain. Tricalcium aluminate is usually not recognized in thin sections because the cubic form is isotropic or because it hydrates early in the hydration history of the concrete forming submicroscopic ettringite or tetracalcium aluminum sulfate hydrate or other tetracalcium aluminum hydrates with or without other anions. These may be visible in voids in older concrete but are best discriminated by X-ray diffraction. - Cement from different sources have different colors of aluminoferrite and the calcium silicates have pale green or yellow or white shades. It should be possible to match cement from one source.	- Normal cement paste consists in plane transmitted light of pale tan matter varying somewhat in the index of refraction and containing relict unhydrated cement grains, ranging down to a few micrometers in maximum size with an upper limit as large as 100 μm in maximum diameter. With crossed polars, the normal paste is black or very dark mottled grey with scattered anhedral poikilitic crystals or small segregations of calcium hydroxide and scattered relict grains of cement. In concrete with high water–cement ratio and siliceous aggregate, the calcium hydroxide crystals are as large as the maximum size of residual cement grains, about 100μm. In concrete with a lower water–cement ratio, higher cement content, and either siliceous or carbonate aggregate, the maximum size of calcium hydroxide crystals is considerably smaller. Regardless of water–cement ratio and type of aggregate, calcium hydroxide crystals occupy space tangential to the undersides of aggregate particles. Where all the aggregate is a carbonate rock, the maximum size of calcium hydroxide is smaller than in comparable concrete with siliceous aggregate. (Calcium hydroxide is probably epitaxial on calcite.) - Cement paste in concrete that has been subjected to prolonged acid leaching and is low in calcium hydroxide which is present as recrystallized virtually anhedral grains precipitated near the exterior surfaces. - In concrete over two or three years old made with Type I, II, or III cement, some ettringite is to be expected as rosettes in air voids. This is a normal phenomenon; to demonstrate sulfate attack it must be established chemically that the SO_3 content of the concrete is greater than would be supplied by the original sulfate content of the cement. Ettringite in voids is not ettringite that has damaged concrete although it may accompany submicroscopic ettringite in the paste that has damaged the concrete.

Table 4.12. Aspects to observe in aggregates for alkali-silica reaction (ASTM C 856, 2020).

Alkali-silica reaction
Does the aggregate contain particles of types known to be reactive (chert, novaculite, acid volcanic glass, cristobalite, tridymite, opal, bottle glass)?
If quartzite, metamorphosed subgreywacke, argillite, phyllite, or any of those listed in the sentence above, are there internal cracks inside the periphery of the aggregate?
Has the aggregate been gelatinized so that it has pulled off during sectioning leaving only a peripheral hull bonded to the mortar?
(This last phenomenon also occurs in concrete with air-cooled slag aggregate, where it indicates a reaction between cement and slag.)
Cracks that appear to be tensile and narrow from the center toward the border of the particle are also evidence of an alkali-silica reaction.

4.2.4. Methods used in the present work

The different methods described above were applied in the study of the various samples presented in the Materials section. Table 4.13 summarizes all the characteristics and equipment used for each method.

The petrographic examination was the first method used to evaluate the potential alkali-reactivity of the aggregates. All the aggregates were first macroscopically separated by fractions based on the colour and texture of the particles; polished thin sections were then prepared by mounting grains representative of each fraction in resin for further characterization under a polarizing microscope followed by a more detailed examination that comprised: (1) Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometry (SEM/EDS); and (2) Electron Probe Microanalysis (EPMA). No point counting was done due to the fine to very fine grain of the rocks. The SEM/EDS and EPMA were performed at the Faculty of Sciences at the University of Lisbon. Several EPMA data were also obtained at Université Laval, Québec city.

Geochemical analyses of representative pulverized samples of the aggregates were performed at the Activation Laboratories, in Canada, by using the Lithium Metaborate/Tetraborate Fusion – ICP and the Inductively Coupled Plasma Mass Spectrometry (ICP/MS) methods.

The potential alkali-reactivity of the aggregates selected for this study was further evaluated by the Accelerated Mortar Bar Test (AMBT) and the Concrete Prism Test (CPT). These tests were conducted both at Université Laval, in Canada, and at LNEC, in the scope of the ReAVA project. The results obtained in this previous research project, concerning the majority of the Azorean aggregates, are critical for comparative purposes with other aggregates and are linked to the theme of the thesis.

Table 4.13. Summary of the methods and equipment used in the present work

Methods	Equipment and conditions
Fraction separation of the aggregates	Identifying compositional differences among the aggregates and separating them by similar rock types from a macroscopic point of view, mainly based on colour and texture
Petrographic examination of aggregates	- Optical microscope: Olympus CX31 polarizing microscope and photomicrographs taken with an Olympus SC100 camera - EPMA in Lisbon: JEOL JXA 8200, coupled with EDS Oxford INCA X-act. The operating conditions of the X-ray tube were current intensity of 10 nA, accelerating voltage of 15 kV, and 1 to 10 μm diameter of the electron beam. The acquisition peak count time was of 20 seconds. - EMPA in Canada: CAMECA SX-100. Column Conditions: Cond 15keV 20nA and beam size of 5 μm. The acquisition peak count time was of 20 seconds.
Geochemical analysis	Activation Laboratories, in Canada, Lithium Metaborate/Tetraborate Fusion – ICP and the Inductively Coupled Plasma Mass Spectrometry (ICP/MS) methods.
AMBT	- Canada (Université Laval): 30 mixtures - In accordance with the standard method CSA A23.2-25A - Aggregate size distribution: 0.15-4.75 mm - Cement type: Cement Québec Type GU with 0.94% $\text{Na}_2\text{O}_{\text{eq}}$ - w/c: 0.50 - Lisbon (LNEC): 13 mixtures - In accordance with the standard method ASTM C 1260 - Aggregate size distribution: 0.15-4.75 mm - Cement type: CEM I 42.5 R with 0.86% $\text{Na}_2\text{O}_{\text{eq}}$ - w/c: 0.47
CPT	- Canada (Université Laval): 31 mixtures (plus a mix of CA + FA) of three prisms each - In accordance with standard method CSA A23.2-14A - Coarse aggregate size distribution: 5-10; 10-14 and 14-20 mm - Fine aggregate size distribution: 0-5 mm - Cement type: Cement Québec Type GU with 0.94% $\text{Na}_2\text{O}_{\text{eq}}$ (boosted to 1.25%, $\text{Na}_2\text{O}_{\text{eq}}$, by cement mass) - Cement content: 420 kg/m^3 - w/c: 0.43/0.44 - Lisbon (LNEC): 13 mixtures of three prisms each - In accordance with RILEM AAR-3 - Coarse aggregate size distribution: 4.75-9.5; 9.5-12.5; 12.75-20 mm - Fine aggregate size distribution: 0-4.75 mm - Cement type: CEM I 42.5 R with 0.86% $\text{Na}_2\text{O}_{\text{eq}}$ - Cement content: 440 kg/m^3 - w/c: 0.43/0.44
DRI	- stereo binocular microscope: Leica S8APO - magnification 16X - on 13 concrete slabs from the CPT performed in Lisbon-LNEC - on 20 concrete slabs from the CPT performed at Université Laval
Petrographic examination of mortar and concrete	Optical microscope: Olympus CX31 polarizing microscope and microphotographs taken with an Olympus SC100 camera
GPT	31 mixes of 2 cylinders each - Concrete cylinders with the same characteristics as CPT

After the completion of the expansion tests, thin sections were prepared from the mortar and the concrete specimens for post-mortem petrographic examination under an optical microscope. The DRI was also performed on selected polished concrete slabs to obtain a quantitative assessment of the condition of the concretes at the end of one year of the CPT method. The concrete mixtures made at Université Laval for the CPT method were also used to produce cylinder specimens, which were cut into slabs to perform the GPT method.

CHAPTER 5

RESULTS

The presentation of the results is done for two different groups of volcanic aggregates: those from islands and those from continental regions. For each region the general geological setting for each aggregate is described and the results obtained by the different test methods presented. The test methods are separated by the ones used in: (1) aggregates; (2) mortar and (3) concrete. Table 5.1 summarizes all the samples studied.

Table 5.1. Country, region and code names were given to the different aggregates studied.

Country	Island/Region		Code Name
Brazil	São Paulo		BRAZ
Canada	Appalachian Region - Quebec		CAN
Iceland	West Iceland		ICL1
	West Iceland		ICL2
	West Iceland		ICL3
	South Iceland		ICL4
Japan	Hokkaido		JAP
Mozambique	Karoo		MOZ
New Zealand	South Island		NZ1
	North Island		NZ2
	North Island		NZ3
Norway	Oslo		NOR
Portugal	Santa Maria		SMA-SM1
	Santa Maria		SMA-SM2
	São Miguel		SMG-SM1
	São Miguel		SMG-SM2
	São Miguel		SMG-SM3
	Terceira		TER-SM1
	Terceira	Azores Archipelago	TER-SM2
	Graciosa		GRA-SM1
	São Jorge		SJO-SM1
	Pico		PIC-SM1
	Faial		FAI-SM1
	Flores		FLO-SM1
	Flores		FLO-SM2
	Corvo		CRV
Spain	Tenerife	Canary Islands	CANY1
	El Hierro		CANY2
Turkey	Izmir		TK
USA	Hawaii		HW1
	Hawaii		HW2
	Hawaii	Hawaiian Islands	HW3
	Hawaii		HW4
	Oahu		HW5
	Oahu		HW6
	Hawaii		HW7

5.1. Sites/samples from Islands

5.1.1. Geological setting

Azores Archipelago (Portugal)

Azores Archipelago is an autonomous Portuguese archipelago formed by nine oceanic volcanic islands and some islets. It is located in the North Atlantic Ocean at about 1600 km from the mainland of Portugal and about 2600 km from the North American Continent. The archipelago extends for about 600 km from Corvo to Santa Maria Islands with a general WNW-ESE trend. The islands are geographically distributed into three groups: 1) the Western group composed of the islands of Flores and Corvo; (2) the Central group comprising the islands of Faial, Pico, São Jorge, Graciosa, and Terceira; and (3) the Eastern group formed by the islands of São Miguel and Santa Maria.

The geological setting is quite complex, but in general terms, the islands emerge from a shallow submarine plateau named Azores Plateau, which is limited by the 2,000 m bathymetric line (Needham and Francheteau, 1974) (Figure 5.1). This plateau has a triangular shape, the western side located to the west of the Mid-Atlantic Ridge (MAR) where the islands of Corvo and Flores are located; the northwest border is defined by the Terceira Rift and the south border by the East Azores Fracture Zone (Lourenço, 2007). MAR is a pure distensive tectonic structure with a general orientation N-S trend, that crosses the archipelago between the islands of Faial and Flores, being intercepted by numerous transform faults along its path. The Azores Plateau is also the site of the Azores Triple Junction (ATJ), where the North American, Eurasian and African plates meet. The MAR corresponds to the western border of the ATJ and the frontier between the Eurasian and African plates corresponds to the Azores-Gibraltar Fracture Zone, that in the area of the Azores Plateau corresponds to a non-linear and more diffuse plate boundary, the “Azores Block” (Lourenço, 2007), extending from the MAR to the GLORIA Fault (Figure 5.1). Moreover, for this area, some authors (Schilling, 1975; Cannat et al., 1999; Lourenço, 2007) argue that there is a magmatic anomaly that corresponds to the Azores hotspot, which is contested by others (e.g. Foulger, 2010).

Santa Maria is the oldest island of the archipelago with about 6 my (millions of years) old (Ramalho et al., 2017) and Pico is the youngest island with a maximum estimated age of about 300 ky (thousands of years) (Nunes, 1999).

In terms of petrology, most of the islands have a full range of compositions, from basic to more evolved rocks like trachyte. Santa Maria, São Jorge, and Pico Islands only have volcanic rocks of basic to intermediate composition: alkali basalts, hawaiites, and mugearites (Larrea et al., 2018).

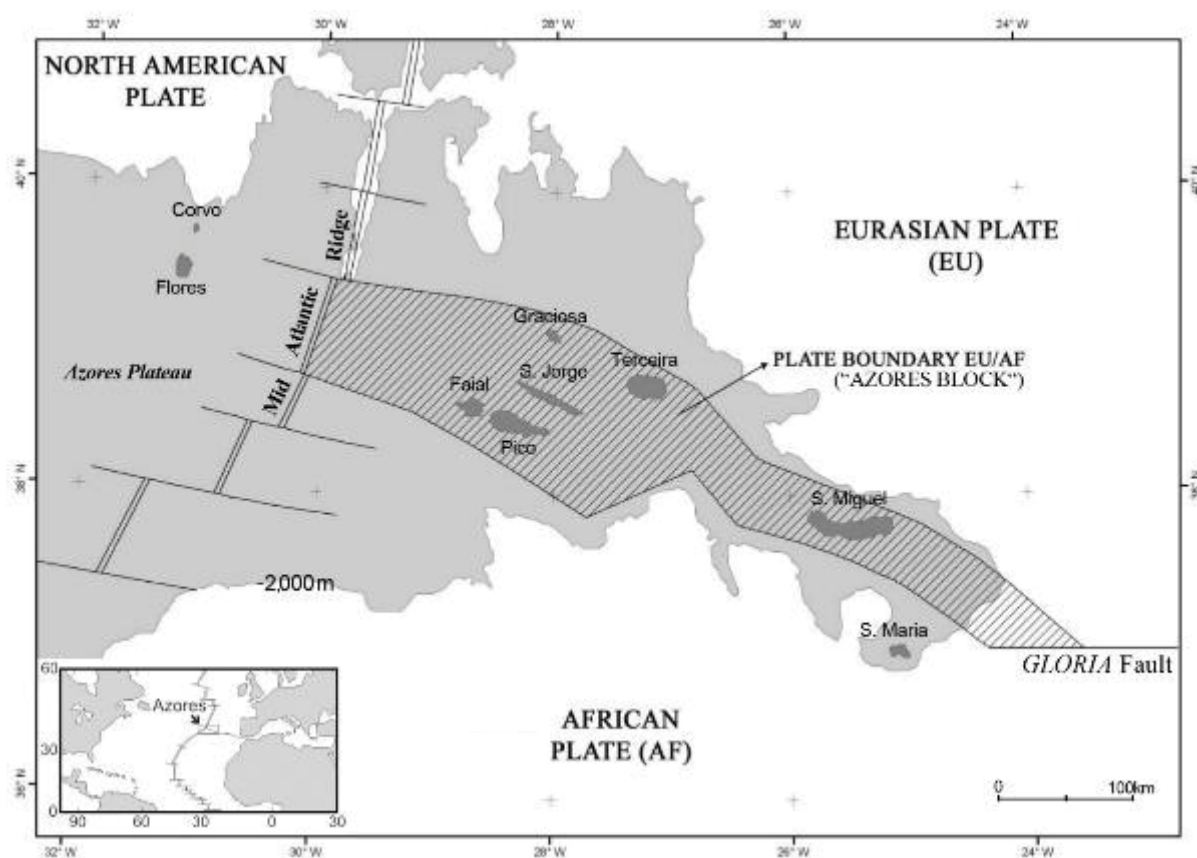


Figure 5.1. General geotectonic setting of Azores Archipelago (Nunes, 2014)

Canary Islands (Spain)

The Canary Islands is an autonomous region of Spain composed of seven volcanic islands: Fuerteventura, Lanzarote, Gran Canaria, Tenerife, La Gomera, La Palma and El Hierro and four smaller islets of La Graciosa, Alegranza, Isla de Lobos and Montaña Clara. It is located in northwest Africa about 100 km from the African coast and about 945 km from the Iberian Peninsula (Portugal, Sagres). The archipelago extends for about 500 km between Alegranza islet and El Hierro Island with a west-southwest to east-northeast trend.

The genesis of the Canary Islands has been the topic of a wide variety of models (Carracedo and Troll, 2016), with its origin being attributed to: (1) a propagating fracture, (2) a local extension ridge, (3) uplifted tectonic blocks, 4) a hot spot and (5) a unifying model (Viñuela, 2007; Hoernle and Carracedo, 2009). The Canary Islands together with the Selvagem Islands form the Canary Volcanic Province (CPV) (Hoernle and Carracedo, 2009) (Figure 5.2) that stands on the oceanic crust of Jurassic age (150-170 my) and developed during the initial stages of the opening of the Atlantic (Carracedo and Troll, 2016). In general, this CPV

decreases in age from the northeast to the southwest which has been interpreted as a hot spot track (Hoernle and Carracedo, 2009).

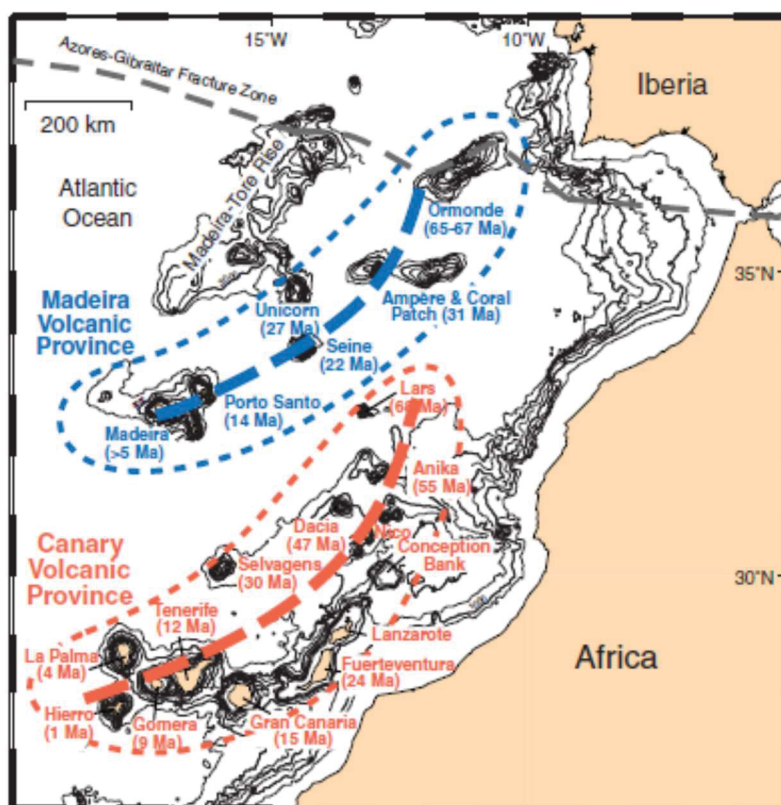


Figure 5.2. The Canary (red) and Madeira (blue) Volcanic Provinces. Thick dashed lines mark the centres of possible hot spot tracks (Hoernle and Carracedo, 2009).

The archipelago is volcanically active being marked by Holocene activity, except for La Gomera Island. (Hoernle and Carracedo, 2009). According to Carracedo and Troll (2016), La Gomera is currently in the postshield erosional stage and the last eruption occurred approximately 2 my ago, Fuerteventura Island is considered extinct with a record of significant Pleistocene eruptions (136 ky ago). In addition, several historical eruptions have occurred in four of the seven islands (Hoernle and Carracedo, 2009; Carracedo and Troll, 2016; Becerril et al., 2016): La Palma, Tenerife, Lanzarote and El Hierro. The composition of the rocks in the Canary Islands is quite diverse and comprises melilitites, nephelinites, basanites, tholeiitic and alkali basalts, tephrites, rhyodacites, rhyolites, pantellerites, comendites, trachytes, phonolites and carbonatites (Viñuela, 2007). According to Carracedo and Troll (2016), Gran Canaria is the island of the entire archipelago that presents the highest variability in terms of rock composition, with lavas of the basanite-basalt to trachyte-phonolite series. Overall, the Canary Archipelago comprises a typical oceanic alkaline suite with saturated and undersaturated end

members, where most basalts are alkaline in the shield-building stages (Viñuela, 2007), occurring also transitional tholeiites (Hoernle and Carracedo, 2009). The trachytes and phonolites are very common in the declining stages (Viñuela, 2007), and in the rejuvenation stages, basanites and nephelinites are the ones essentially formed (Viñuela, 2007; Hoernle and Carracedo, 2009).

Hawaiian Islands (USA)

The Hawaiian Islands are located in the North Pacific Ocean at 3,765 km from North America and 3,350 km from the Archipelago of Marquesas. The archipelago belongs to a chain of peaks that, together with the Emperor chain, forms the Hawaiian-Emperor volcanic chain that stretches almost 6,000 km along the Pacific Ocean. This geological feature comprises 107 main central volcanoes, which are progressively younger towards the southeast of the chain, and with still-active volcanoes (Clague and Dalrymple, 1987).

The Hawaiian Archipelago itself comprises two groups of islands: (1) eight main islands (Nihau, Kauai, Oahu, Molokai, Lānai, Maui, Kahoolawe, and Hawaii) and several islets, located in the southeastern part; and (2) atolls together with small volcanic and coral islands in the northwestern part.

The volcanic ridge (Figure 5.3) is delimited by a symmetrical depression, which is 0.7 km deeper than the surrounding ocean floor and is called the Hawaiian Deep. The Hawaiian hotspot volcanism is a melting anomaly that has been building volcanoes for the past 70 my leaving a trail of volcanoes behind and forming a new central volcano as the Pacific oceanic plate moves on top of the hotspot (Clague and Dalrymple, 1987).

According to Clague and Dalrymple (1987), the Hawaiian volcanoes have four different stages in their evolution, based on the chemistry of the magma:

- (1) preshield, which represents the volcano growth with steep slopes of pillow lavas and a shallow summit caldera;
- (2) shield, that corresponds to the construction of the main volcanic edifice with tholeiitic basaltic lava flows;
- (3) postshield, characterized by the covering of the volcano with alkali basaltic lavas and associated differentiated lava;
- (4) rejuvenated, where periods of quiescence and erosion are interrupted by small eruptions from isolated vents.

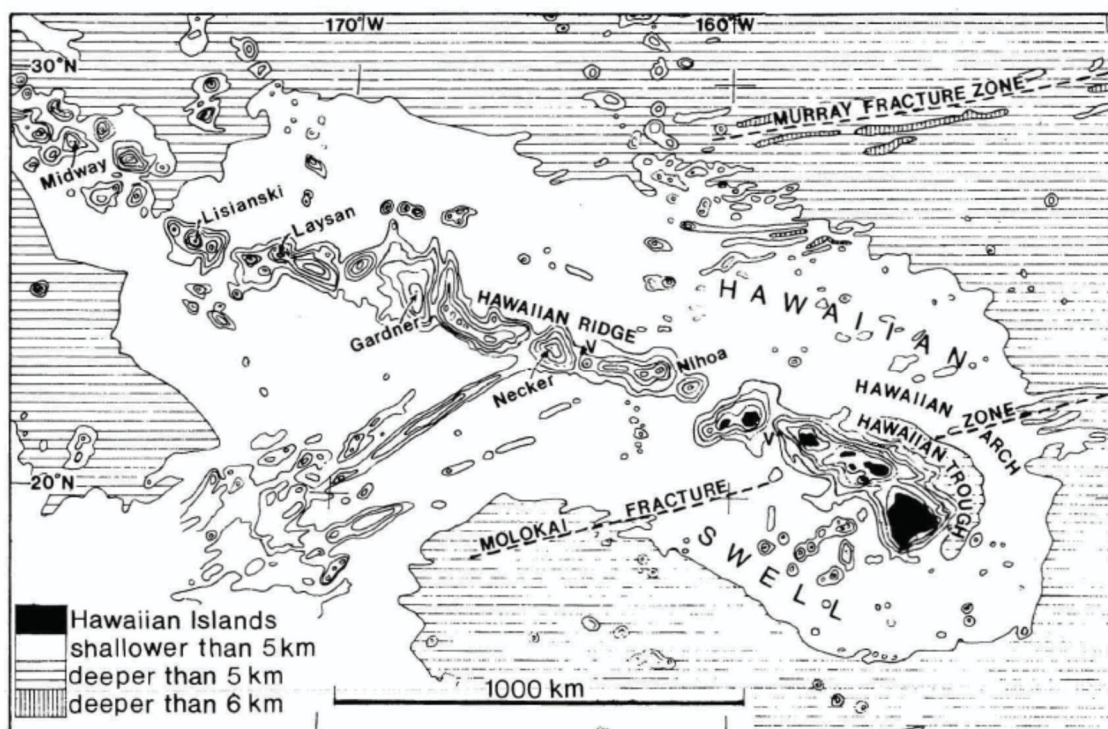


Figure 5.3. Geotectonic setting of Hawaiian Islands (Walker, 1990).

All the major islands have in common the tholeiitic basalts. Regarding the alkali basalt, it is present in all of the islands except Lānai Island (Clague and Dalrymple, 1987). The islands of Oahu, Maui, and Hawaii range in composition from basanites to trachytes. As to Kauai and Molokai Islands, these range from basanites to mugearites or benmoreites, respectively. The other two islands, Nihau and Kahoolawe, have a clear limited predominance of tholeiitic and alkaline basalts, with hawaiiites being part of the last one. Oahu has the most silicic lava composition of the Hawaiian Islands, with 68% of SiO_2 corresponding to rhyodacite (Sherrod et al., 2007).

Iceland

Iceland is an island located in the North Atlantic Ocean halfway between Europe and Greenland/North America with the northernmost parts touching the Arctic Circle. Beyond the limit of the island, there are the skerries (e.g. small islets) of Kolbeinsey and Hvalbakur, and also Vestmannaeyjar or Westman Islands where Surtsey is the more recent island. The shortest distance is to Greenland with more or less 285 km, being also distanced from other locations such as Norway at approximately 970 km, Faeroe Islands at about 435 km and Scotland at around 805 km.

Iceland is situated at the intersection of two large submarine structures: (1) the Mid-Atlantic Ridge (MAR) which separates the North American plate from the Eurasian plate and (2) the

Greenland-Iceland-Iceland Faroes Ridge (Thordarson and Höskuldsson, 2014) (Figure 5.4). This ridge is also known as Greenland-Scotland Transverse Ridge (GSTR) in accordance to Denk et al., (2011), which is a series of ridges that connects Greenland, Iceland and Faroe Islands and continues to the United Kingdom (Eiríksson et al., 2021).

According to Thordarson and Höskuldsson (2014), Iceland is a part of the oceanic crust that forms the floor of the Atlantic Ocean, being the surface expression of a hotspot (Denk et al., 2011). The mantle plume that produces this hotspot has been changing its position through time (Thordarson and Höskuldsson, 2014) and it is believed that 60-50 my ago the mantle plume was situated under East Greenland (Denk et al., 2011).

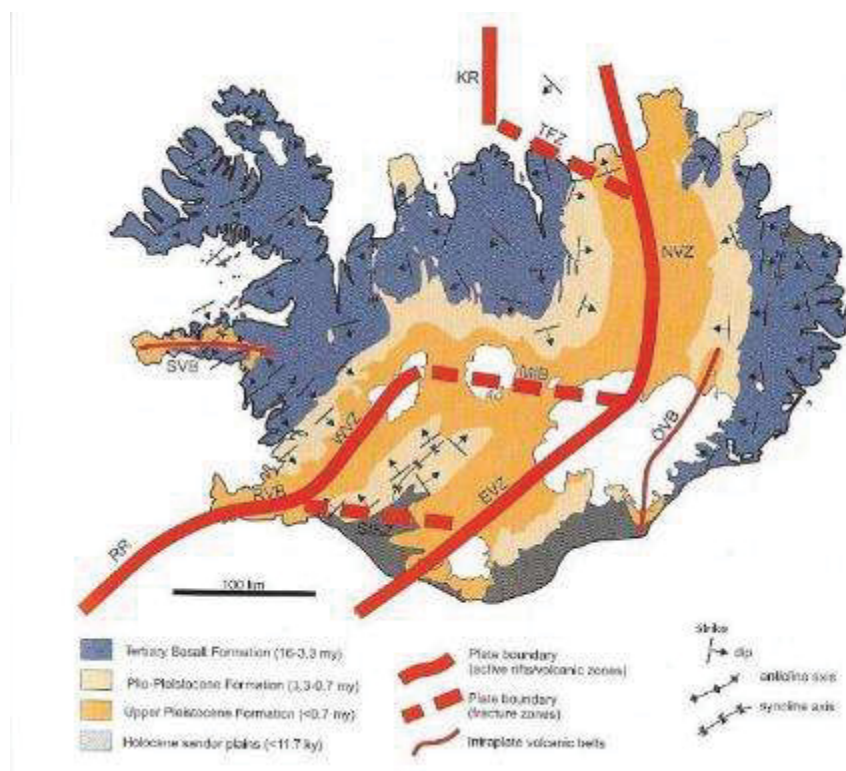


Figure 5.4. Geotectonic setting of Iceland. (Thordarson and Höskuldsson, 2014). RR: Reykjanes Ridge; RVB: Reykjanes Volcanic Belt; WVZ: West Volcanic Zone; MIB: Mid-Iceland Belt; EVZ: East Volcanic Zone; NVZ: North Volcanic Zone; SISZ: South Iceland Seismic Zone; TFZ: Tjörnes Fracture Zone; KR: Kolbeinsey Ridge; ÖVB: Öræfi Volcanic Belt and SVB: Snæfellsnes Volcanic Belt.

In Iceland, the segments of the Mid Atlantic Ridge are represented by the junction between the Reykjanes ridge in the south and the Kolbeinsey ridge in the north, and its in-land expression corresponds to narrow belts of active faulting and volcanism extending from Reykjanes, in the southwest, to Öxarfjörður, in the north, being the only section of the MAR exposed above sea level (Thordarson and Höskuldsson, 2014). Besides the major volcanic zones, there are two active intraplate volcanic zones: (1) Öræfi Volcanic Belt located to the

east of the mantle plume and (2) Snæfellsnes Volcanic Belt in the west, which sits on the mantle plume trail and is partly superimposed on an extinct volcanic zone (Thordarson and Höskuldsson, 2014; Eiríksson and Símonarson, 2021).

The oldest rocks of Iceland belong to the Tertiary Basalt Formation with a period from 16 to 3.3 my ago and occur in the easternmost and westernmost parts of the island while the youngest rocks occur along the rifting zone with an age less than 700 ky (Thordarson and Höskuldsson, 2014).

The majority of the rocks exposed in Iceland are igneous, 90% of them being mafic and the rest are intermediate or felsic (Thordarson and Höskuldsson, 2014). The igneous rocks are predominantly volcanic (Denk et al., 2011) containing mainly basaltic rock types (Sveinsdottir and Wigum, 2003). Other volcanic rocks include andesite and rhyolite (Thordarson and Höskuldsson, 2014). Intrusive plutonic rocks also occur in Iceland, especially in the western part, which is composed of gabbros and granophyres (Upton and Wright, 1961), and in the southwest part, with gabbro xenoliths (Gurenko and Sobolev, 2006). Sedimentary rocks are also present but they represent a small part when compared to igneous rocks. According to Eiríksson et al. (2021), there are thick layers of sediments intercalated with lava sequences. The same authors recognize littoral and sublittoral sandstones with abundant marine fossils, peats and lacustrine mudrocks, diamictites (e.g. unstratified and chaotic deposits containing large angular stones and boulders floating in a matrix of sand to clay-size material - Thordarson and Höskuldsson, 2014) and conglomerates with marine fossiliferous deposits. In addition, sand or “sandur” (sand in Icelandic) occupies large parts of the Iceland landscape, especially in the southern parts of the island (Figure 5.4) (Sveinsdottir and Wigum, 2003). They are known as sandy deserts and together they form a surface of over 20,000 km² (Arnalds et al., 2001; Arnalds, 2010). The sand is originated mainly from glacial margins, glacio-fluvial deposits and subglacial volcanic eruptions (with “*jökulhlaups*”-forming eruptions), but also sedimentary rocks; these areas have a black colour due to their basaltic origin and are often dominated by the volcanic glass (Arnalds et al., 2001).

The basalts in Iceland belong to two magma series: (1) alkaline, which occurs in the off rift volcanic zones, and (2) tholeiitic, which occurs in the mid-Atlantic rift zone where it transects the island (Sigmarsson and Steinthórsson, 2007).

Japan

Japan is an archipelago formed by four main islands (Hokkaido, Honshu, Kyushu and Shikoku) (Yamada et al., 2011) and more than 3500 smaller islands (Petry, 2003). It is located, in the northern hemisphere, off the east coast of Asia about 160 km from South Korea, 300 km

from Russia and 730 km from China (distances measured from the main islands of Japan). The archipelago stretches over 3,000 km with a general northeast to southwest trend.

The Japanese Archipelago is located in the active volcanic belt of the Circum Pacific Rim with a complex geological structure (Yamada and Miyagawa, 2017) as a result of the interaction of three plates, the Eurasian, Pacific, and Philippine Sea plates, which meet at an unstable trench-trench-trench triple junction in the Pacific Ocean offshore of central Japan, known as the Boso triple junction (Van Horne et al., 2017) (Figure 5.5). The archipelago forms a volcanic arc system, as a result of the subduction of the oceanic Pacific and Philippine Sea plates under the continental plate of Eurasia (Van Horne et al., 2017). The arc system includes four different domains (Taira, 2001; Taira et al., 2016): (1) the Western Kuril-eastern Hokkaido arc, (2) the western Hokkaido-Honshu arc, (3) the Ryukyu arc and (4) the Izu-Ogasawara (Bonin) Arc. The Sea of Japan forms a continent-ocean back-arc system (Van Horne et al., 2017) that started to open in Miocene times (Jolivet et al., 1991), through the movement of plates, intra-arc rifting and back-arc spreading (Van Horne et al., 2017). According to Jahn (2010), the Japanese Islands represent a segment of a 450 my old subduction-related orogen along the western Pacific convergent margin, where most tectonic units are composed of late Palaeozoic to Cenozoic accretionary complexes. The same author refers that the Japanese orogenic complex is known as “Nipponides,” and is composed mainly of Permian to recent subduction-accretion complexes with very few fragments of the older continental crust.

Japan has been built by accretionary tectonics, large-scale metamorphism, magmatism and volcanism, thus where various types of rocks are present including surface sediments, metamorphic, plutonic and volcanic rocks. According to Taira (2001), these lithologies, separated by ages include: (1) Pre-Jurassic units with Palaeozoic ophiolites, sedimentary rocks, metamorphic rocks, and granitic rocks; (2) Permian to Jurassic accretionary prisms that include high-pressure/temperature metamorphic rocks and cover sequences; (3) Cretaceous to Tertiary accretionary prisms and cover sequences; (4) Jurassic to Tertiary igneous rocks and (5) Neogene and Quaternary igneous and sedimentary rocks. According to Yamada and Miyagawa (2017), andesites are in the north-western part of the inter pacific volcanic belt, various metamorphic rocks are located in its western part and a wide range of metamorphic and sheared rocks (such as mylonite or cataclasite) occur in the south-western part. According to Katayama and Kaneshige (1986), the Cenozoic Japanese volcanic rocks are widely distributed in the country, the andesite being the major source of volcanic aggregates. Besides andesite, also basalt, dacite and rhyolite can be found, belonging to the calc-alkaline, alkaline (Wakita, 2013) and tholeiitic volcanic suites (Ohba et al., 2009).

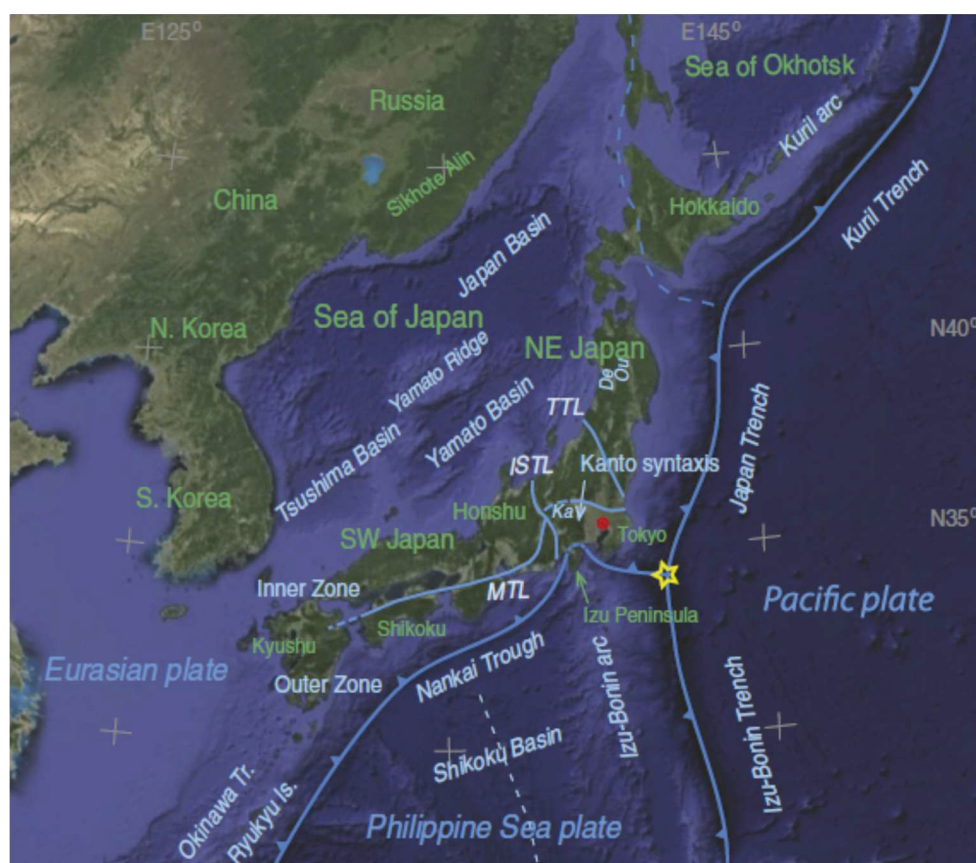


Figure 5.5. Geotectonic setting of Japan. Yellow star: Boso triple junction. Light blue lines, major inland faults (Van Horne et al., 2017). MTL: Median Tectonic Line; ISTL: Itoigawa-Shizuoka Tectonic Line; TTL: Tanakura Tectonic Line; Ka: Kanto Mountains; De: Dewa Hills; Ou: Ou Backbone Range.

New Zealand

New Zealand is an archipelago formed by three main islands: North Island, South Island and Stewart Island (which is much smaller, compared with the other two), and several inhabited and uninhabited smaller islands. It is located in the southwest Pacific Ocean, at about 1,400 km southeast of Australia and is considered the emergent part of a continental fragment “Zealandia” (Campbel and Landis, 2009). The main islands stretch for about 1,500 km in a more or less northeast-southwest orientation.

It lies along the Circum Pacific “ring of fire” belt, in the southwest boundary of the Indo-Australian and Pacific plates (Shayan and Freitag, 2017). This boundary extends from the southern end of the Tonga–Kermadec Trench and runs down offshore of the eastern coast of the North Island, cuts across the upper half of the South Island along the Hope Fault, and then connects with the Alpine Fault on the western side of the Southern Alps, and heads offshore at the entrance of Milford Sound (western Fiordland) and into the Puysegur Trench (Campbel and Landis, 2009). This convergent margin at the North Island makes the Pacific plate to

subduct under the Indo-Australian plate causing volcanic activity located mostly in the northern and central North Island (Shayan and Freitag, 2017) where continental rifting is occurring (e.g. Taupo Volcanic Zone - TVZ) (Campbel and Landis, 2009). The tectonics in the North Island is dominated by subduction at the Hikurangi Trough, back-arc rifting in the TVZ, and strike-slip faulting in the eastern North Island dextral fault belt (Wallace et al., 2004). The same authors say that in the South Island the plate margin is marked by the Alpine Fault where the plates passed each other horizontally, as strike-slip faulting, with the Marlborough Fault System and the Alpine Fault accommodating most of the Australia-Pacific relative motion. In the south of New Zealand, the Australian plate plunge below the Pacific plate, this is the reverse of what is occurring on the North Island (Campbel and Landis, 2009). Thus, according to Campbel and Landis (2009), the main islands of New Zealand are the result of tectonic uplift, localized tectonic down drop or subduction-related volcanism as a result of a collision between the Pacific Plate and the Indo-Australian Plate. Figure 5.6. shows the geological setting of New Zealand.

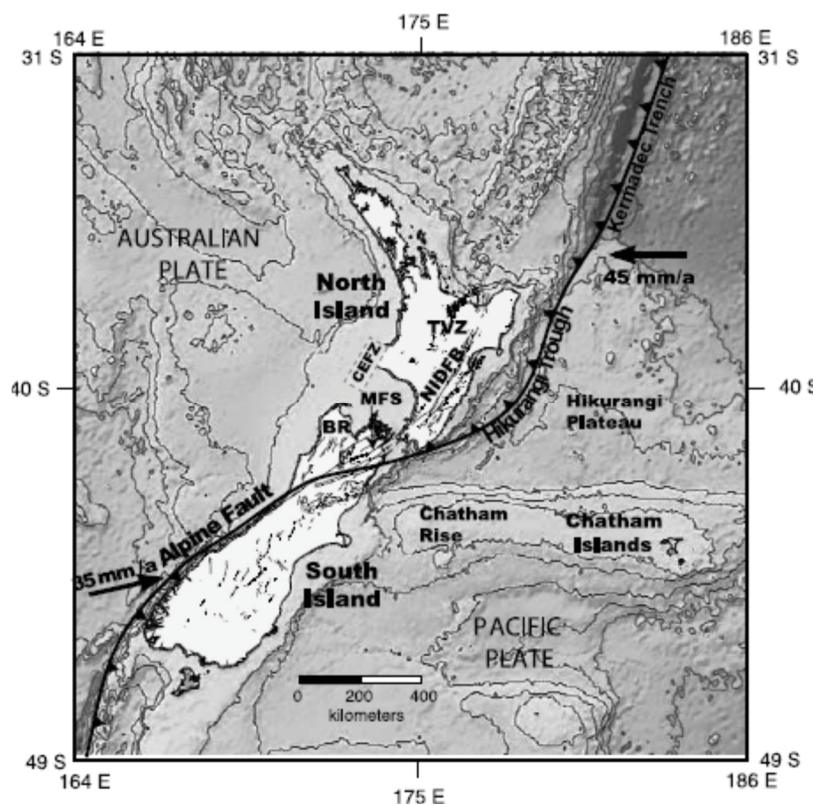


Figure 5.6. Tectonic setting of New Zealand. (Wallace et al., 2004).

In New Zealand, the three types of rocks can be found: igneous, metamorphic and sedimentary, greywacke being probably the dominant sedimentary rock (described as muddy sandstone or silty sandstone), and schists are the main metamorphic rock (Campbel and

Landis, 2009). Regarding the igneous rocks, some plutonic rocks such as diorite, gabbro and granite are also present, being observed on Stewart Island as dykes (Ballance, 2017). Rhyolite, andesite, dacite and basalt are among the volcanic rocks present in New Zealand, that according to Shayan and Freitag (2017) are located predominantly on the North Island.

5.1.2. Characterization of volcanic aggregates from Islands

5.1.2.1. Geochemical analysis, TAS diagram and CIPW norm

Geochemical analyses of the aggregates were performed at the Activation Laboratories (ACTLABS), in Canada, by using the lithium metaborate/tetraborate fusion–ICP and ICP/MS method. Table 5.2 shows the results obtained, which were plotted in a TAS diagram (Le Bas et al., 1986) by using the free software GCDKit3.00. The gravel samples from Iceland were not analyzed because of the heterogeneity in lithology present in the particles.

The chemical composition of all the aggregates has some differences regarding the content of SiO₂. The SiO₂ content in the Azores Archipelago is in majority lower than 50%, ranging from 43% to 48.5% except for the samples of TER-SM1 (65%), FLO-SM2 (52%) and FLO-SM1 (53%), which are more evolved rocks. The samples from the Canary Islands and Iceland also show values of SiO₂ content lower than 50%. Regarding New Zealand, only one of the samples has a SiO₂ content slightly higher than 50% (NZ3 = 50.2% wt.). The Japan sample is an andesite, which has a higher content of SiO₂ (~60%). As for the Hawaiian Islands, the SiO₂ content is higher than 50% in the majority of the aggregates (HW1, HW3, HW4, HW5, HW6 and HW7), with only one sample undersaturated (HW2, 46.6%).

Regarding LOI, the highest contents are found for the samples from Azores Archipelago: (1) SMA-SM1 (2.15%) and SMA-SM2 (3.25%). These values indicate that there is some degree of alteration of these rocks.

The oversaturation, saturation and under saturation in silica are defined by certain normative minerals for the basalts that, according to Yoder and Tilley (1962), follow certain conditions. The CIPW norm (Table 5.3), calculated from the bulk chemical composition of each sample, indicates that some of the Hawaiian basalts are considered oversaturated in silica because they have normative quartz and hypersthene, namely HW3, HW5, HW6 and HW7 samples. Other basalts are considered undersaturated in silica as they contain normative hypersthene and olivine, namely the samples from Iceland (ICL3), New Zealand (NZ2 and NZ3) and some from the Hawaiian Islands (HW1 and HW4). On the other hand, and based on the same concept as Yoder and Tilley (1962), most of the samples from the Azores (except

TER-SM1), the samples from the Canary Islands and one sample from New Zealand (NZ1) are considered alkaline basalts because they contain normative nepheline and olivine.

The alkali-silica diagram (TAS) (Figure 5.7) shows that the volcanic rocks studied from the different islands range mostly between basalts and trachybasalts. There are also some basanites, andesite, two basaltic trachyandesite, a trachyandesite and a trachyte.

Table 5.2. Bulk chemical composition of the island volcanic aggregates.

Major Oxides (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ total	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	SUM total
SMA-SM1	43.31	12.98	11.88	11.05	11.52	3.62	0.76	2.29	0.42	0.17	2.15	100.20
SMA-SM2	43.55	13.28	12.16	9.96	11.75	2.80	0.57	2.40	0.62	0.19	3.25	100.50
SMG-SM1	47.25	14.09	12.20	8.06	9.16	3.25	2.04	3.48	0.61	0.16	-0.20	100.10
SMG-SM2	46.45	14.08	12.87	8.19	9.39	3.11	1.89	3.59	0.65	0.18	-0.49	99.92
SMG-SM3	45.69	13.36	12.26	8.00	10.75	2.90	1.68	3.41	0.67	0.17	-0.63	98.26
TER-SM1	64.79	13.92	6.10	0.65	0.71	6.35	4.97	0.61	0.07	0.22	1.13	99.51
TER-SM2	48.54	14.65	12.12	6.82	10.88	3.09	0.97	3.11	0.59	0.17	-0.10	100.80
GRA-SM1	47.70	16.76	11.11	7.15	9.58	3.82	1.36	2.74	0.56	0.17	-0.73	100.20
SJO-SM1	45.73	15.39	12.82	8.58	10.07	3.22	1.07	3.51	0.53	0.17	-0.47	100.60
PIC-SM1	48.00	14.93	11.29	8.04	10.51	3.32	1.21	2.69	0.44	0.17	-0.64	99.94
FAI-SM1	48.53	16.35	11.39	6.26	9.36	3.91	1.69	2.92	0.62	0.17	-0.55	100.60
FLO-SM1	53.36	16.40	8.37	2.15	5.65	5.65	2.73	1.84	0.67	0.24	3.16	100.20
FLO-SM2	51.66	16.58	9.06	3.29	7.08	4.66	2.55	2.43	0.93	0.22	0.64	99.10
CRV	49.81	16.15	10.85	4.96	8.34	4.26	1.85	2.70	0.71	0.17	-0.32	99.47
CANY1	45.94	16.89	11.18	4.03	8.99	4.76	1.85	3.07	0.21	0.17	1.40	99.85
CANY2	44.13	13.70	13.38	9.46	9.77	3.51	1.49	3.54	0.79	0.19	0	99.73
ICL3	47.67	14.89	13.54	8.07	11.57	2.16	0.15	1.78	0.15	0.20	-0.50	99.78
JAP	59.72	16.06	7.90	3.51	7.07	2.69	1.57	0.63	0.10	0.15	0.4	99.90
NZ1	41.95	14.60	13.97	7.10	10.86	3.76	1.61	3.33	0.89	0.21	1.30	99.79
NZ2	48.93	16.97	10.65	7.27	12.12	2.29	0.34	0.98	0.11	0.17	-0.10	99.81
NZ3	50.17	15.56	9.90	9.15	10.33	2.48	0.55	1.07	0.24	0.17	0	99.79
HW1	50.31	12.88	11.96	10.38	9.75	2.06	0.38	1.93	0.20	0.16	-0.40	99.77
HW2	46.60	13.73	13.04	10.43	11.01	2.27	0.69	1.89	0.21	0.18	-0.50	99.77
HW3	52.11	13.83	11.81	6.98	10.5	2.27	0.38	2.06	0.21	0.16	-0.60	99.83
HW4	54.22	17.25	9.59	2.74	5.06	5.38	2.51	1.58	1.04	0.22	0	99.92
HW5	51.62	14.18	11.31	7.06	9.25	2.58	0.39	2.06	0.25	0.15	0.90	99.84
HW6	51.21	14.28	11.54	7.39	9.23	2.54	0.32	2.05	0.25	0.15	0.70	99.82
HW7	50.87	13.55	12.48	7.17	10.20	2.32	0.44	2.19	0.24	0.17	0	99.81

The TAS fields of trachybasalt, basaltic trachyandesite and trachyandesite can be subdivided, classifying further the rocks according to $\text{Na}_2\text{O} - 2.0 \geq \text{K}_2\text{O}$ or $\text{Na}_2\text{O} - 2.0 < \text{K}_2\text{O}$ (Le Maitre et al., 2002). These happen only for some of the samples from the Azores Archipelago (SMG-SM1, SMG-SM2, GRA-SM1, FAI-SM1, FLO-SM1, FLO-SM2 and CRV) and a Hawaiian Islands sample (HW4). According to these authors, the line between the foidite

field and the basanite–tephrite field indicates that further criteria must be used to separate these types. In this case, the calculation of normative olivine (> 10 %) (Table 5.3) allows us to classify the studied rocks as basanites and not tephrites. For the field of trachyte/trachydacite, another criterion must be followed according to the function $100 * Q / (Q + an + ab + or)$: if the value is less than 20% the rock is a trachyte; if greater than 20% it is a trachydacite (Le Maitre et al., 2002). In the studied rocks, the value is lower than 10%, thus the rock is a trachyte.

Table 5.3. Calculation of the CIPW norm (wt. %) for the island's volcanic aggregates.

Normative minerals	Q	Pl	Or	Ne	Di	Hy	Ol	Ac	Il	Mt	Ap	Total
SMA-SM1	0.0	21.78	4.55	14.47	31.09	0.0	21.39	0.0	4.43	1.32	1.00	100.0
SMA-SM2	0.0	33.27	3.49	7.39	27.07	0.0	21.30	0.0	4.69	1.33	1.48	100.0
SMG-SM1	0.0	36.19	12.00	4.86	19.25	0.0	18.28	0.0	6.57	1.44	1.41	100.0
SMG-SM2	0.0	35.78	11.11	4.97	19.09	0.0	19.29	0.0	6.78	1.48	1.51	100.0
SMG-SM3	0.0	32.96	10.05	5.69	25.2	0.0	16.50	0.0	6.53	1.51	1.58	100.0
TER-SM1	7.78	44.61	29.84	0.0	2.71	9.64	0.0	2.40	1.18	0.0	0.16	100.0
TER-SM2	0.0	48.05	5.67	0.46	21.95	0.0	15.22	0.0	5.85	1.46	1.34	100.0
GRA-SM1	0.0	45.23	7.98	6.00	15.7	0.0	17.41	0.0	5.15	1.26	1.27	100.0
SJO-SM1	0.0	40.76	6.26	5.55	17.91	0.0	20.35	0.0	6.59	1.36	1.20	99.98
PIC-SM1	0.0	42.28	7.09	4.2	21.94	0.0	17.09	0.0	5.07	1.30	1.02	99.99
FAI-SM1	0.0	44.39	9.87	5.44	16.55	0.0	15.49	0.0	5.47	1.38	1.41	100.0
FLO-SM1	0.0	54.45	16.61	3.48	10.77	0.0	8.12	0.0	3.59	1.38	1.60	100.0
FLO-SM2	0.0	54.05	15.31	1.62	10.41	0.0	10.4	0.0	4.69	1.35	2.18	100.0
CRV	0.0	49.56	10.93	3.26	14.31	0.0	13.71	0.0	5.15	1.42	1.65	99.99
CANY1	0.0	36.80	11.23	13.26	20.57	0.0	10.07	0.0	6.00	1.58	0.51	100.0
CANY2	0.0	27.93	8.81	10.28	21.31	0.0	21.63	0.0	6.72	1.49	1.83	100.0
ICL3	0.0	48.62	0.89	0.0	21.38	9.17	14.86	0.0	3.38	1.36	0.35	100.0
JAP	14.15	50.13	9.34	0.0	6.14	17.82	0.0	0.0	1.20	1.01	0.23	100.0
NZ1	0.0	22.10	9.69	15.56	25.14	0.0	17.27	0.0	6.42	1.73	2.09	100.0
NZ2	0.0	54.45	2.01	0.0	20.11	8.13	12.09	0.0	1.86	1.12	0.25	100.0
NZ3	0.0	50.86	3.25	0.0	16.35	15.17	10.78	0.0	2.03	1.00	0.56	100.0
HW1	0.0	42.18	2.25	0.0	18.18	26.99	5.11	0.0	3.67	1.17	0.46	100.0
HW2	0.0	41.50	4.08	1.56	22.9	0.0	24.61	0.0	3.59	1.28	0.49	100.0
HW3	2.96	45.43	2.25	0.0	19.99	23.65	0.0	0.0	3.89	1.35	0.49	100.0
HW4	0.0	61.22	14.89	0.0	2.44	2.62	12.04	0.0	3.02	1.36	2.41	100.0
HW5	2.38	48.32	2.30	0.0	15.26	25.94	0.0	0.0	3.95	1.26	0.58	99.99
HW6	1.69	48.57	1.89	0.0	14.57	27.5	0.0	0.0	3.93	1.26	0.58	99.99
HW7	1.10	45.04	2.60	0.0	19.72	25.41	0.0	0.0	4.18	1.41	0.56	100.0

Q=quartz; Pl=plagioclase; Or= Orthoclase; Ne=Nepheline; Di= Diopside; Hy=Hypersthene; Ol=Olivine; Ac=Acmite; Il=Ilmenite; Mt=Magnetite; Ap=Apatite

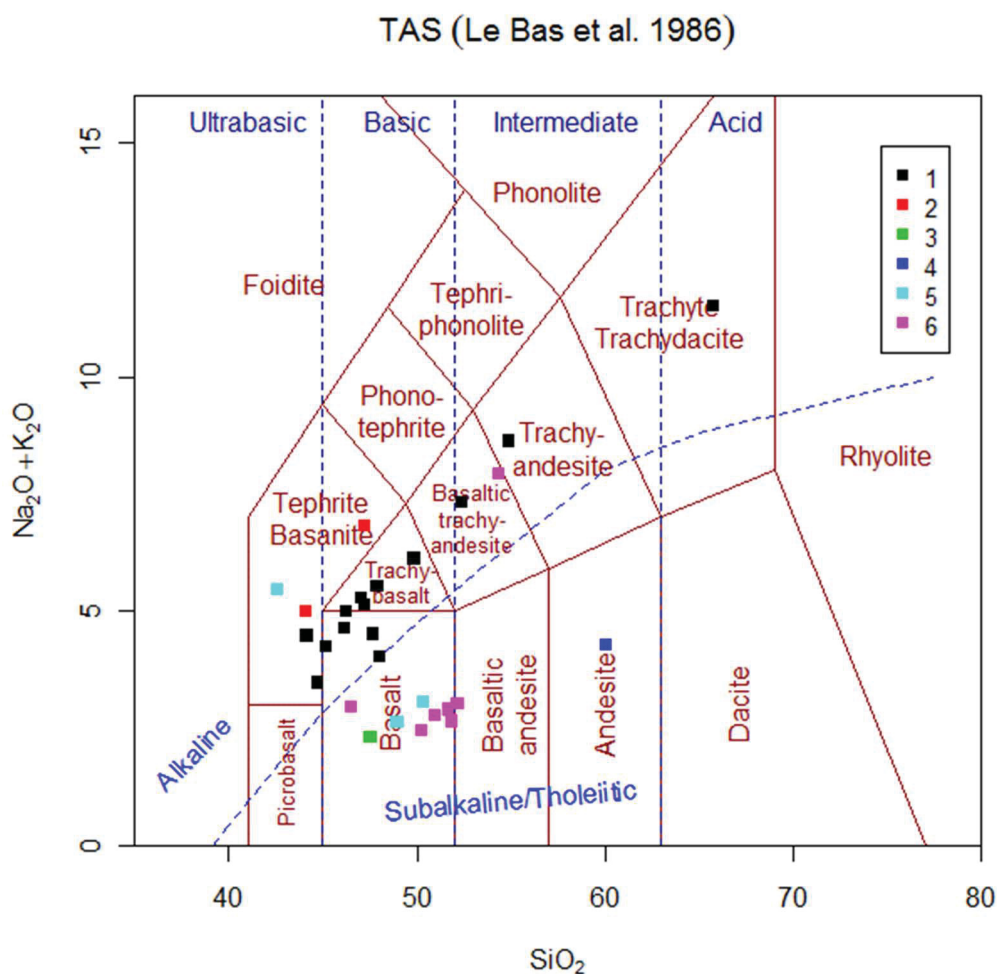


Figure 5.7. TAS diagram (after Le Bas et al., 1986) of the volcanic aggregates from different islands: 1 - Azores Archipelago (Portugal), 2 - Canary Islands (Spain), 3 - Iceland, 4 - Japan, 5 - New Zealand and 6 - Hawaiian Islands (USA).

The chemical classification of the rocks obtained by the TAS diagram is summarized in Table 5.4.

From the TAS diagram, it is also possible to classify the rocks into alkaline or subalkaline/tholeiitic magma series. The studied rocks from the Azores belong all to the alkaline series, and the same happens to the two rocks from the Canary Islands, one from the Hawaiian Islands (HW4) and one from New Zealand (NZ1). The other samples fall in the subalkaline/tholeiitic magma series. According to the diagram AFM (Figure 5.8) from Irvine and Baragar (1971), only the Japan sample belongs to the calc-alkaline series; the Hawaiian samples HW1, HW2, HW3, HW5, HW6 and HW7, the Iceland sample ICL3 and the New Zealand samples NZ2 and NZ3 all follow a tholeiitic trend.

Table 5.4. Chemical classification of each rock sample based on the TAS diagram.

Island	Sample	Chemical classification	Island	Samples	Chemical classification
Azores (Portugal)	SMA-SM1	Basanite	Canary (Spain)	CANY1	Basanite
	SMA-SM2	Basanite		CANY2	Basanite
	SMG-SM1	Pot tb/Basalt (tb)	Hawaiian Islands (USA)	HW1	Basalt
	SMG-SM2	Potassic basalt (tb)		HW2	Basalt
	SMG-SM3	Basalt		HW3	Basalt
	TER-SM1	Trachyte		HW4	Mugearite (Bta)
	TER-SM2	Basalt		HW5	Basalt
	GRA-SM1	Hawaiiite (tb)		HW6	Basalt
	SJO-SM1	Basalt		HW7	Basalt
	PIC-SM1	Basalt	Iceland	ICL3	Basalt
	FAI-SM1	Hawaiiite (tb)	Japan	JAP	Andesite
	FLO-SM1	Benmoreite (ta)	New Zealand	NZ1	Basanite
	FLO-SM2	Mugearite (Bta)		NZ2	Basalt
	CRV	Hawaiiite (tb)		NZ3	Basalt

tb: trachybasalt; Bta: basaltic trachyandesite; ta: trachyandesite

AFM plot (Irvine and Baragar 1971)

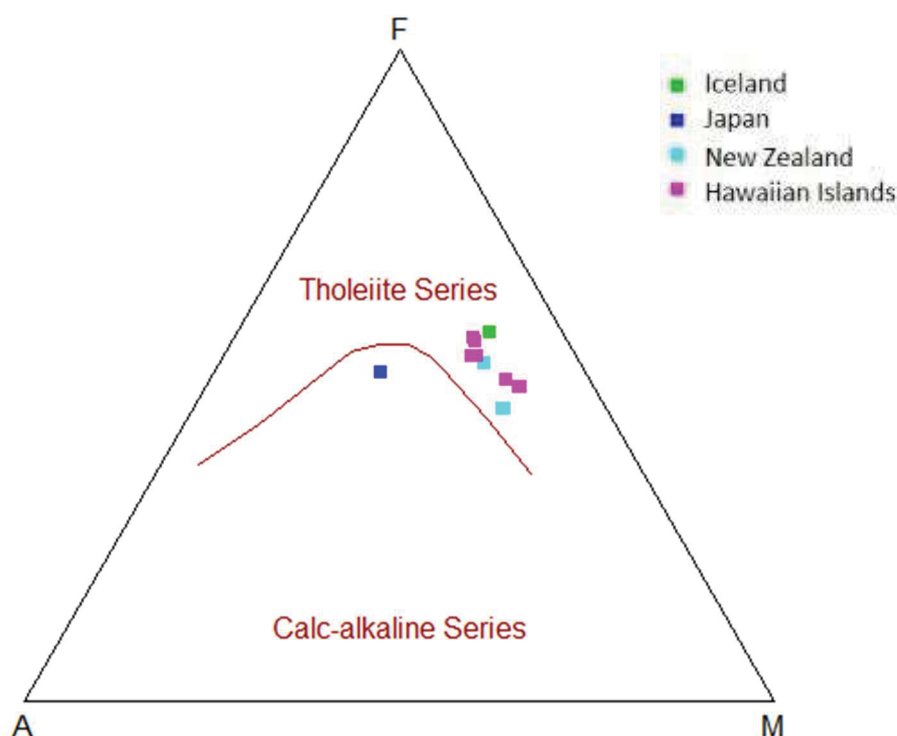


Figure 5.8. AFM diagram (after Irvine and Baragar, 1971) of the studied volcanic aggregates belonging to the subalkaline/tholeiitic magma series. A = $\text{Na}_2\text{O} + \text{K}_2\text{O}$; F = $\text{FeO} + 0.8998 \text{Fe}_2\text{O}_3$; M = MgO (wt.%).

5.1.2.2. Petrographic examination

For the petrographic study of the samples of the aggregates, different scales were used, starting with the microscopic observation of the grains and the separation in different fractions, depending on the texture and the colour. The petrographic examination of the thin sections of the aggregates was performed by using a polarizing microscope, complemented by EPMA-WDS or EDS spectrometry whenever necessary. In the following text, a summary is made of the lithologies identified, their texture and mineral composition.

Azores Archipelago (Portugal)

Macroscopically, the rock samples from Azores Archipelago are aphanitic; some are aphyric (TER-SM1, FLO-SM2) or sub-aphyric (FAI-SM1, FLO-SM1) and others contain a high amount of phenocrysts (SMG-SM1, SMG-SM2, SMG-SM3, PIC-SM1). The phenocrysts are usually of olivine and pyroxene, and less frequently of plagioclase; iddingsite is also visible in some of the rock samples (SMA-SM2, SMG-SM1). The samples are grey in colour, some display reddish tones (SMA-SM2, FLO-SM1) and only one has a greenish tone and is banded (TER-SM1). The samples are massive in texture and only one has a more vesicular texture (SJO-SM1) (Figure 5.9). CRV is the only sample studied as aggregate particles of crushed rock, instead of a block.

Under the polarizing microscope, these samples show mainly porphyritic texture with phenocrysts of euhedral to subhedral habit set in an intergranular groundmass. Olivine, pyroxene and plagioclase form the most common phenocrysts, with variable abundance from sample to sample. Overall, the matrix of the samples presents the same mineral assemblage with the presence of opaque minerals (titanomagnetite and ilmenite), apatite, and sometimes biotite. Most of the samples show some oriented texture where the plagioclase microlites are arranged in a sub-parallel mode in the groundmass (pilotassitic texture) (Figure 5.10 A).

Carbonates (possibly calcite) are also present in some samples (SMA-SM1, FLO-SM1), in crystals scattered in the matrix, especially in the vicinity of the phenocrysts of the other minerals, filling cracks inside the crystals or in veins in the rock (Figure 5.10B). In some rocks, olivine phenocrysts show a brownish-red iddingsite rim of variable thickness (SMA-SM1, SMA-SM2), which is more pronounced in the SMA-SM2 sample (Figure 5.10 C). Also, in one of the samples (SMA-SM1), a mineral with low relief and low interference colour that is filling the vesicles of the rock is observed, which was identified by SEM/EDS analysis in previous work (Medeiros (2011) as a zeolite (analcime) (Figure 5.10 D).



Figure 5.9. Block samples of the Azorean rocks were used as aggregates. Only the CRV sample is formed by crushed aggregate.

From the point of view of mineralogy and texture, the sample of trachyte (TER-SM1) is markedly distinct from the others (Figure 5.10 E). It contains sparse large crystals mainly of anorthoclase and small crystals of the same mineral, and also albite, biotite, and opaque minerals. The groundmass contains plagioclase and anorthoclase, aegirine, augite, aenigmatite, opaque minerals, apatite and sporadic brownish volcanic glass. Besides, the presence of silica in the matrix was detected by SEM/EDS (Medeiros, 2011). This silica form is preferentially located near the phenocrysts. The rock exhibits a trachytic texture.

The presence of volcanic glass is scarce in the studied rock samples. It was only identified in three samples (SMG-SM1, TER-SM1, TER-SM2), either as interstitial glass (Figure 5.10F) or as inclusions in phenocrysts. Also, a quartz xenocryst was identified in the SMG-SM1 sample.

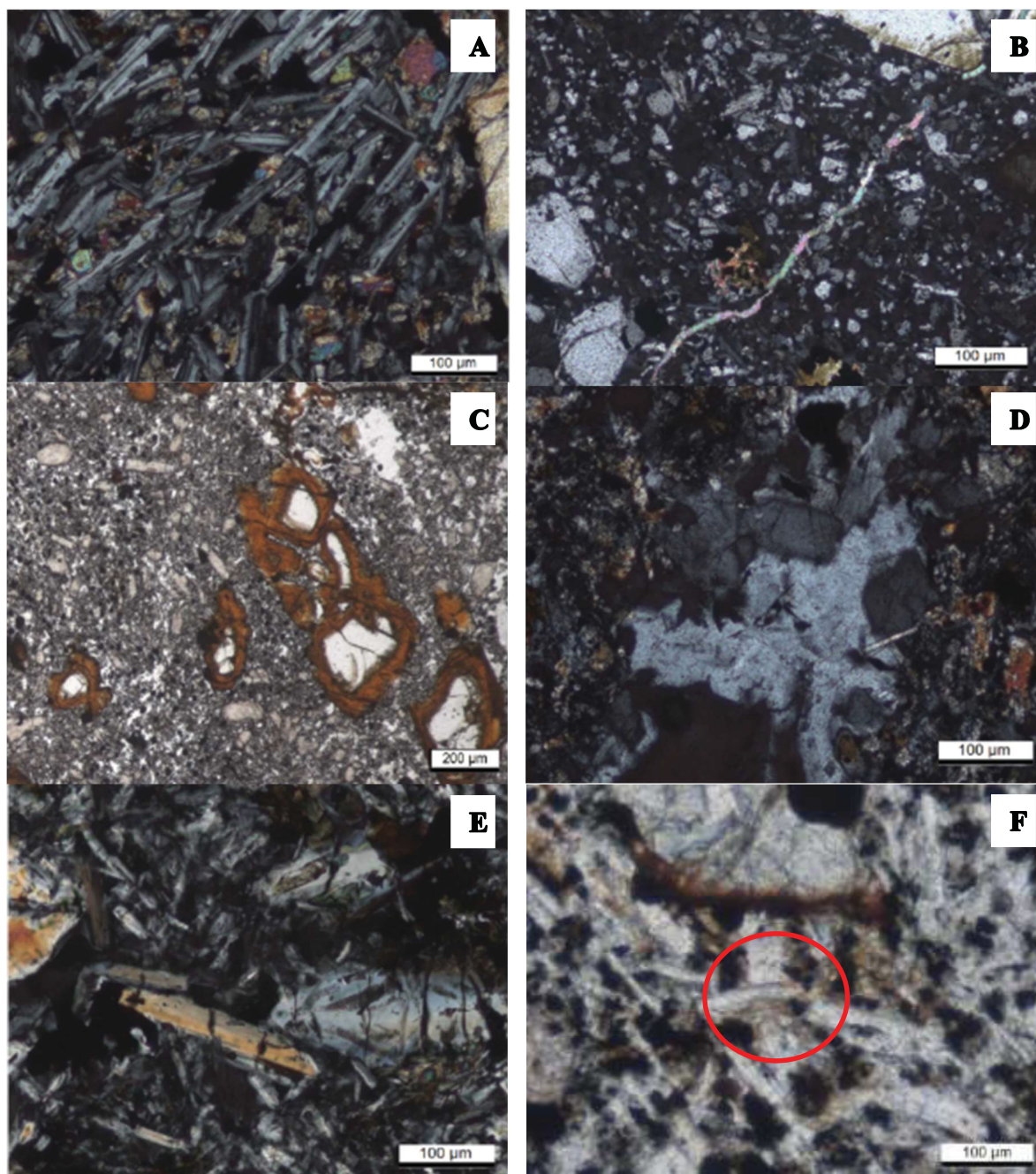


Figure 5.10. Photomicrographs of Azorean aggregates. Photo A, B, D and E in XPL; C and F in PPL. A) Basalt with pilotassitic groundmass (TER-SM1); B) Calcite filling a crack (SMA-SM1); C) Iddingsite rims in olivine crystals (SMA-SM2); D) Analcime filling a vesicle (SMA-SM1); E) Anorthoclase crystals in the trachyte sample (TER-SM1), and F) Interstitial volcanic glass (SMG-SM1).

Canary Islands (Spain)

From the macroscopic point of view, both samples are aphanitic, one is subaphyric with very few phenocrysts of pyroxene (CANY1) and the other contains phenocrysts mainly of olivine and pyroxene and less of plagioclase (CANY2). The samples range in colour from grey to a reddish tone and display either massive or vesicular texture. The shape of the particles of crushed aggregate is elongated with sub-angular grains. Both samples were separated into three fractions each, based on the colour and the texture: almost massive, vesicular and reddish particles (Figure 5.11).



Figure 5.11. Canary samples of aggregate in crushed rock are split into different fractions according to the texture and colour.

The two samples from the Canary Islands correspond to basanite with vesicles in some of the aggregate particles. Despite having the same type of rock, there are some differences in terms of texture.

In the thin section, the CANY1 sample is subaphyric (Figure 5.12A) with rare phenocrysts of clinopyroxene (Figure 5.12B and C) and opaque mineral and shows microphenocrysts of clinopyroxene and plagioclase set in a microlitic groundmass of plagioclase, opaque minerals, iddingsite and clinopyroxene. One of the aggregate particles presents several areas with a high concentration of volcanic glass in the matrix. Olivine crystals are completely replaced by iddingsite with a red-brownish colour and some clinopyroxene (augite) shows peculiar extinction displaying an hourglass structure. Carbonates (calcite) appear sometimes scattered in the matrix. Also, zeolite occurs, as identified by EPMA analysis (Table 5.5), in one of the particles, forming a yellowish mineral with low interference (Figures 5.12D and Figure 5.13).

Interstitial brownish volcanic glass is present in some sections of the rock sample (Figures 5.12E and 5.14), which quantitative composition is defined by EPMA results (Table 5.6). Biotites occur randomly in the groundmass (Figure 5.12F).

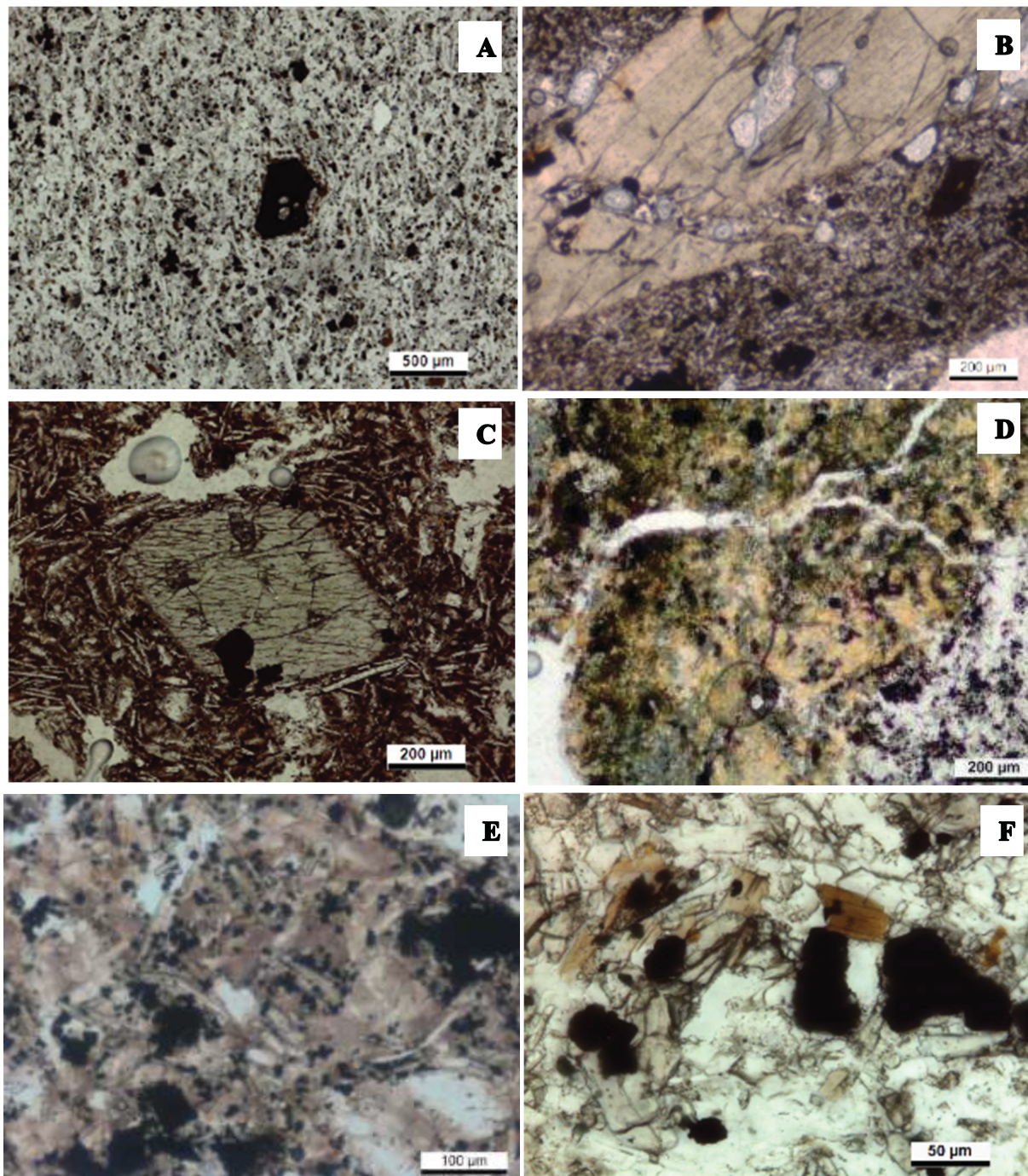


Figure 5.12. Photomicrographs of sample CANY1. All photos are in PPL. A) Subaphyric texture; B) and C) Phenocryst of clinopyroxene; D) Presence of zeolite; E) Interstitial volcanic glass (brownish, amorphous); F) biotite.

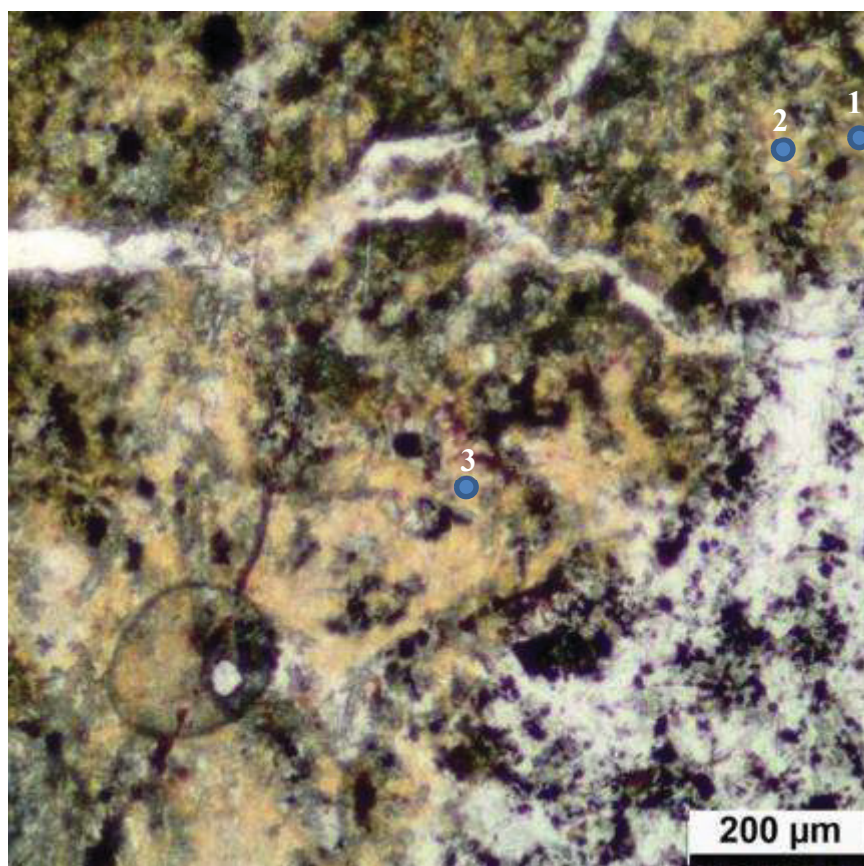


Figure 5.13. Sample CANY1: yellowish mineral and location of the EPMA analyses.

Table 5.5. Sample CANY1 EPMA-WDS results concerning the composition of a yellowish zeolite crystal whose composition is compatible with natrolite (Figure 5.13).

Oxides (%)	1	2	3
SiO ₂	52.14	50.14	47.39
TiO ₂	0.20	0.10	0.14
Al ₂ O ₃	31.77	32.42	27.34
FeO	2.00	2.46	4.61
MnO	b.d.l.	b.d.l.	b.d.l.
MgO	0.31	0.22	0.38
CaO	b.d.l.	b.d.l.	b.d.l.
Na ₂ O	13.70	13.53	13.90
K ₂ O	3.47	3.92	4.20
Total	103.6	102.77	97.98

b.d.l. = below detection limit

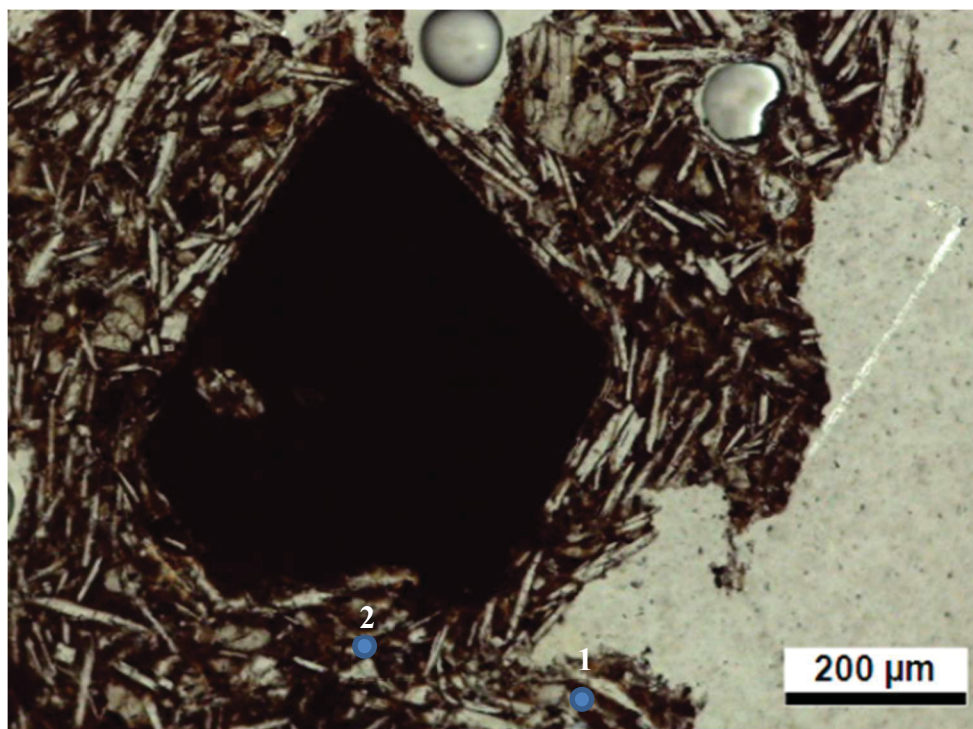


Figure 5.14. Sample CANY1. Volcanic glass and respective examination points.

Table 5.6. Sample CANY1 EPMA-WDS results of the dark-brown volcanic glass in Figure 5.14.

Oxides (%)	1	2
SiO ₂	49.88	43.66
TiO ₂	2.65	4.45
Al ₂ O ₃	7.32	8.73
FeO	7.03	8.31
MnO	0.31	0.17
MgO	10.79	11.58
CaO	16.78	21.63
Na ₂ O	1.60	0.58
K ₂ O	1.04	b.d.l
Total	97.45	99.14

b.d.l = below detection limit

The CANY2 sample is porphyritic with phenocrysts of olivine, clinopyroxene and plagioclase immersed in an intergranular groundmass (Figure 5.15A). The matrix is characterized by the presence of plagioclase, clinopyroxene and opaque minerals. Olivine crystals display embayments and skeletal textures (Figure 5.15B). In some aggregate particles, plagioclase shows a peculiar texture that looks like roots, sieve texture, growing inside the crystal (Figure 5.15C). Clusters of plagioclase phenocrysts form glomeroporphyritic textures that are visible in some aggregate particles. In some sections, several vesicles are filled with carbonates (Figure 5.15D) and others with zeolites, as confirmed by EDS (Figure 5.16). Volcanic glass is scarce in this sample.

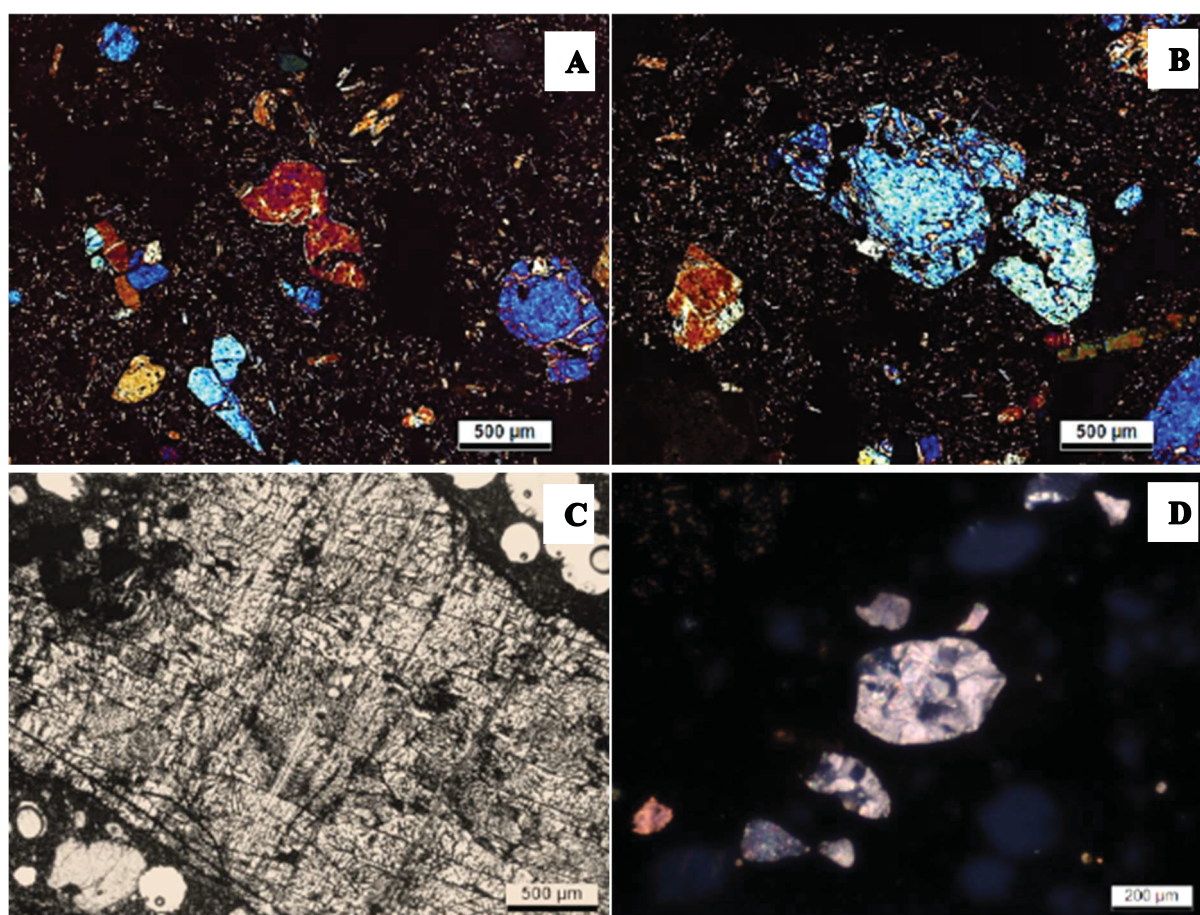


Figure 5.15. Photomicrographs of sample CANY2: A, B and D in XPL, C in PPL A) Vesicular and porphyritic texture; B) Skeletal olivine; C) Plagioclase with peculiar sieve-like texture; D) Vesicles filled with carbonate minerals.

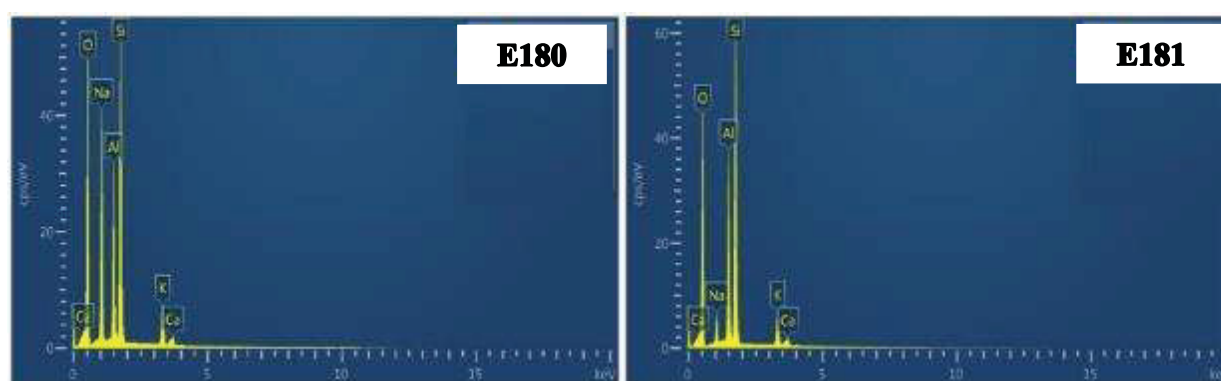
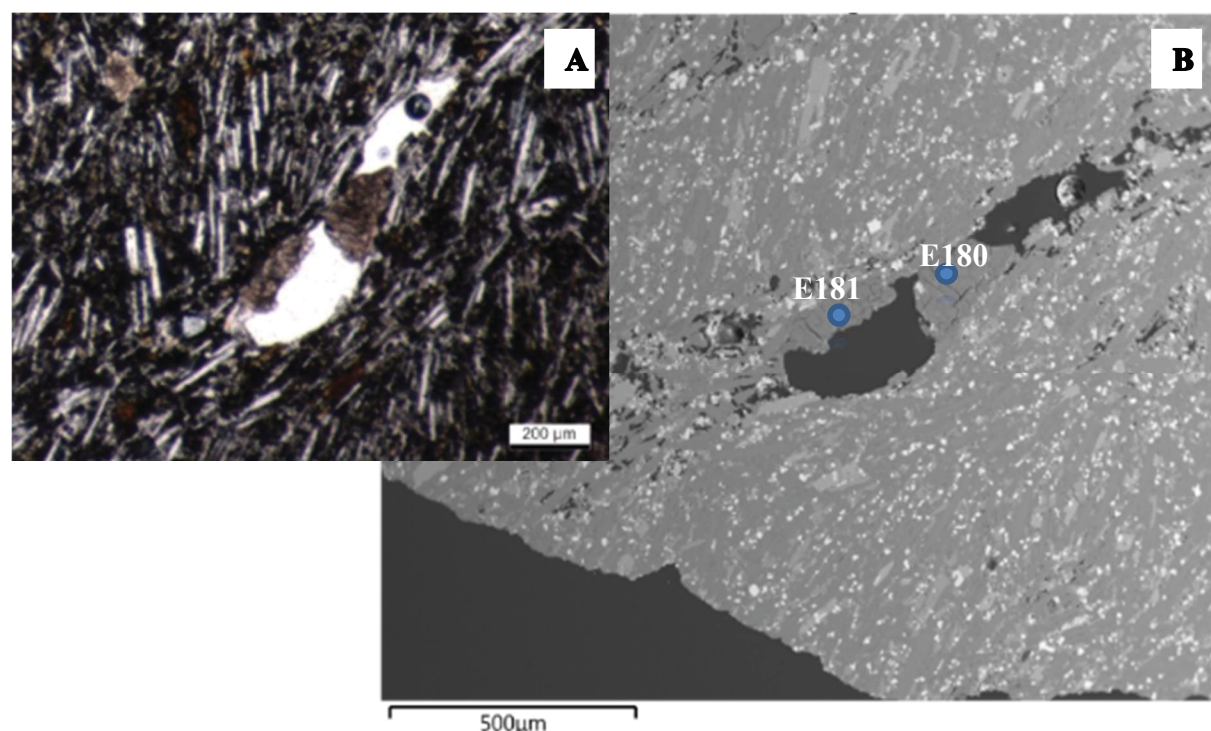


Figure 5.16. Sample CANY2. Photomicrograph (A) and BSE image (B) and respective EDS spectra of zeolite partly filling a void (E180 and E181).

Hawaiian Islands (United States of America)

Macroscopically, the aggregates from two of the Hawaiian Islands are aphanitic; some contain olivine phenocrysts (HW1, HW2 and HW7), in one there are rare olivine phenocrysts (HW3) while the others are completely aphyric (HW4, HW5 and HW6). The majority of the samples are light grey in colour to a slightly reddish tone but one of the samples is more reddish when compared to the others. They are massive to vesicular with rounded to elongated and subangular particles. The various samples were grouped into different facies: almost massive, vesicular and reddish particles. Figure 5.17 shows the hand sample of each aggregate.



Figure 5.17. Macroscopic photos of the different aggregates and facies from Hawaiian aggregates.

In the thin section, the samples of the Hawaiian aggregates are porphyritic to poorly porphyritic, with a fine-grained intergranular to intersertal groundmass. Variolitic texture (Figure 5.18A) is also present in certain aggregate particles where some skeletal plagioclase laths with fans of dendritic clinopyroxene are visible. Some aggregate particles show a subophitic texture with plagioclase laths embedded in clinopyroxene minerals (HW1, HW2, HW5).

The majority of the samples contain phenocrysts mainly of olivine (HW1, HW2, HW4, HW6 and HW7), sometimes of plagioclase (HW2 and HW7) and more rarely of clinopyroxene (HW1 and HW7) as well as microphenocrysts of olivine and plagioclase (HW1, HW2, HW4, HW5, HW6 and HW7) and sometimes of clinopyroxene or orthopyroxene (HW5 and HW6). The matrix is constituted, in general, by the same mineral assemblage, opaque minerals and in different aggregate particles volcanic glass is present (HW1, HW2, HW3, HW5, HW6 and HW7). In the particles exhibiting subophitic texture, plagioclase and clinopyroxene are the dominant minerals but glass can occur. In one of the samples the coexistence and transition of two different textures, porphyritic and subophitic, is observed (HW2).

Euhedral to subhedral olivine crystals are common in the majority of the samples, with some exhibiting disequilibrium features (e.g., embayments and skeletal habit) (Figure 5.18B and

5.18C). In some samples (HW5 and HW6), the olivine crystals show a brownish-red iddingsite rim and in one sample (HW1) it presents peculiar features where spinel resembles roots growing inside the olivine crystals (Figure 5.18D). Clinopyroxene (e.g. augite) sometimes shows hourglass structure (HW2) and is occasionally twined (HW7). Orthopyroxene is also present but only in two samples (HW5 and HW6). Orthopyroxene occurs in prismatic crystals with no pleochroism and with parallel extinction (Figure 5.18E). Skeletal morphologies in the opaque minerals are also common in the analysed samples. Some of the samples show monomineralic glomeroporphyritic clusters of olivine (Figure 5.18F) or plagioclase as well as clusters of plagioclase, olivine and clinopyroxene minerals. The presence of carbonates (calcite) was only identified in the HW4 sample; it is scattered irregularly throughout the different aggregate particles that constitute the sample. Brownish volcanic glass (Figure 5.19A, B, C, D, E and F) is observed as interstitial glass (HW1, HW2, HW3, HW5, HW6 and HW7) (Figure 5.19A, B and F) or dispersed as irregular patches of vesicular glass containing minute particles of iron ore and needles of apatite and spinel enclosed in the glass (HW3, HW5 and HW6), (Fig. 5.19C, D and F). Volcanic glass composition was confirmed by EPMA. The same techniques were also used for identifying some minerals that constitute the rock samples.

The EDS spectra and also the use of EPMA analysis in some of the Hawaiian samples were performed especially in volcanic glass, clay minerals and some different features of the samples.

In the HW1 sample, the EPMA confirmed the composition of volcanic glass (Table 5.7) in one of the aggregate particles (Figure 5.20).

In sample HW3, volcanic glass present was identified by EPMA (Figure 5.21 and Table 5.8).

In sample HW5, EPMA was also used to identify the composition of an isotropic yellowish-brown material (Table 5.9) that was scattered in the groundmass of the aggregate particle (Figure 5.22).

For the HW6 sample, the presence of vesicular volcanic glass was confirmed by EPMA (Figure 5.23 and Table 5.10).

Regarding the HW7 sample, the presence of volcanic glass in different aggregate particles was analysed and confirmed by EPMA (Figure 5.24 and 5.25; Tables 5.11 and 5.12).

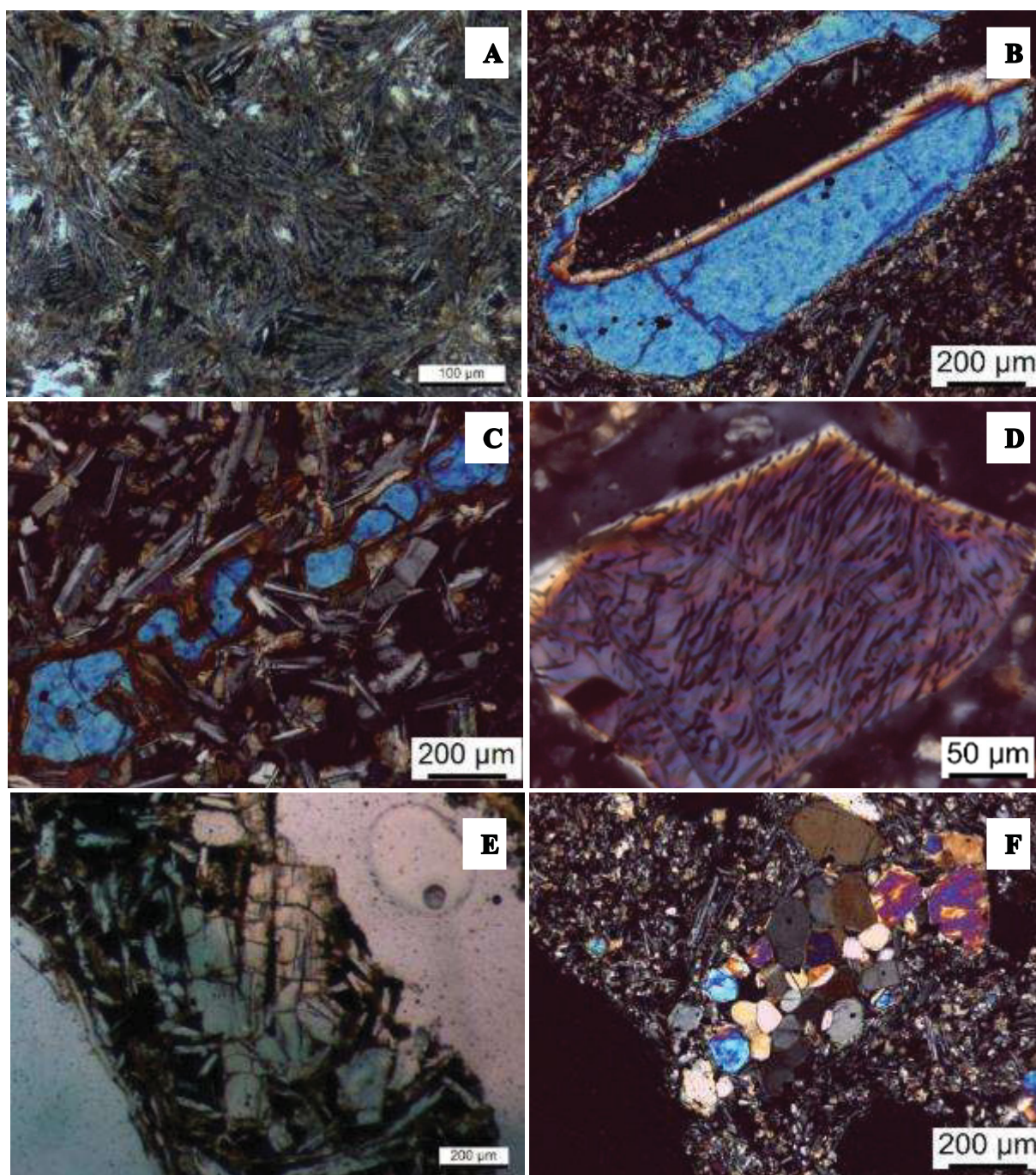


Figure 5.18. Photomicrographs of Hawaiian samples: B, C, D and F in XPL, A and E in PPL. A) Variolitic texture (HW5); B) Embayed olivine (HW1); C) Skeletal olivine rimmed by iddingsite (HW5); D) Olivine with peculiar textures (HW1); E) Orthopyroxene crystals (HW6); F) Glomeroporphyritic clusters of olivine (HW2).

The results in Table 5.8 are very low and must be considered only indicative of the element composition. The presence of reactive forms of silica was confirmed in all samples by polarizing microscopy and EPMA.

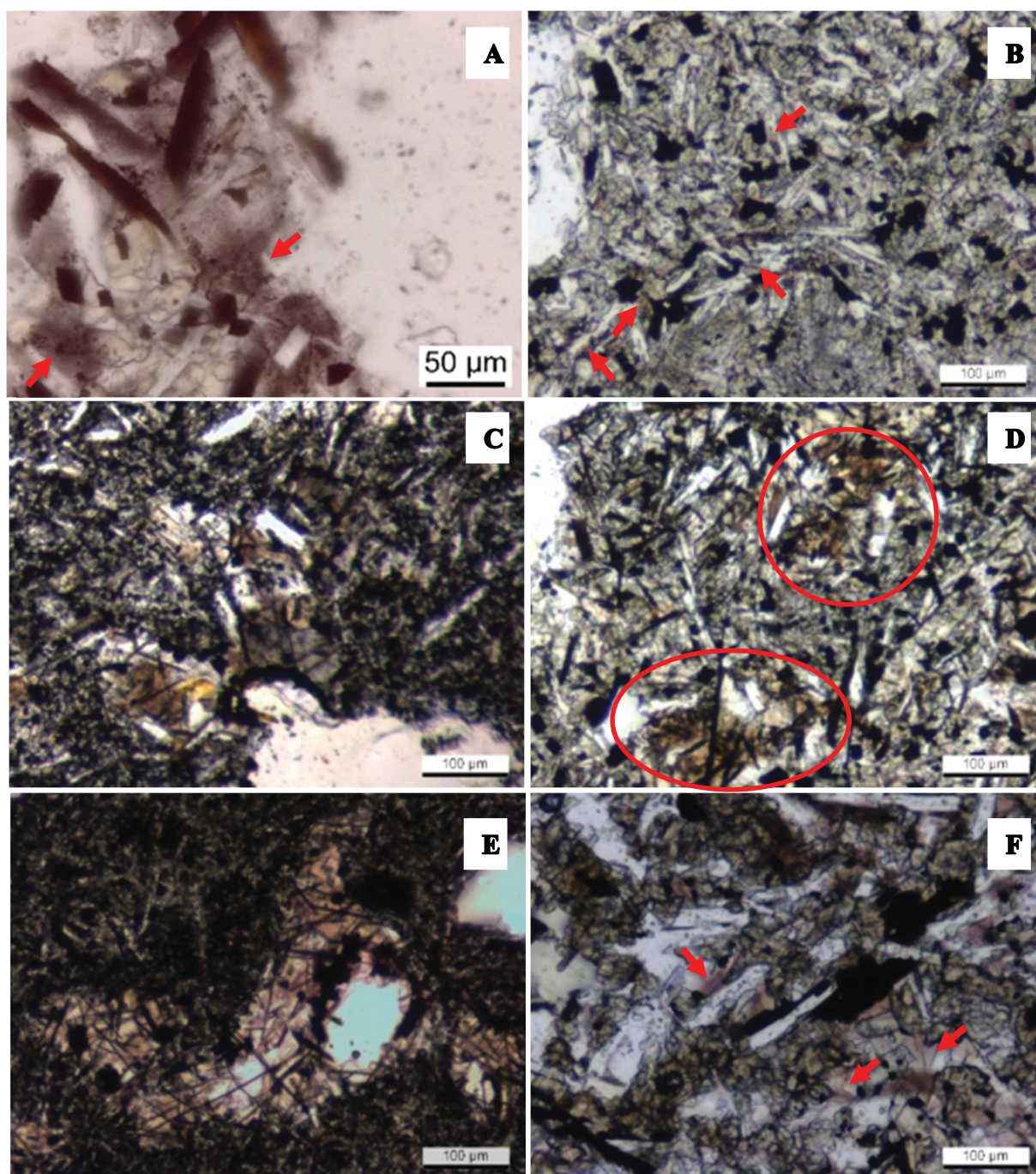


Figure 5.19. Photomicrographs of brownish volcanic glass in the Hawaiian samples. The red arrows point to the interstitial brownish volcanic glass and the red circles to the vesicular glass. All photos are in PPL. A) Interstitial volcanic glass in HW1 sample; B) Interstitial volcanic glass in HW3 C) Vesicular glass containing minute crystals of iron ore and needles of apatite in HW3; D) Vesicular glass containing minute particles of iron ore and needles of apatite in HW5; E) Vesicular glass containing minute particles of iron ore and needles of apatite in HW6; F) Interstitial volcanic glass in HW7.

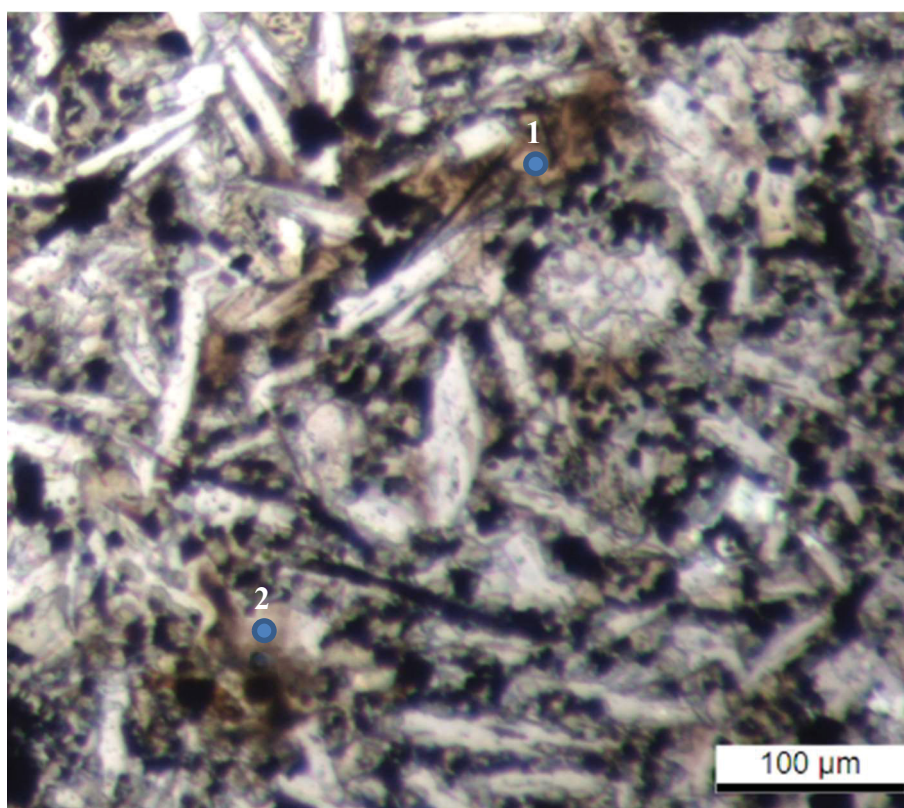


Figure 5.20. Sample HW1. Brownish volcanic glass and respective examination points.

Table 5.7. Sample HW1.EPMA-WDS results of the analyses of volcanic glass.

Oxides (%)	1	2
SiO ₂	80.49	79.12
TiO ₂	0.71	0.66
Al ₂ O ₃	11.71	12.55
FeO	0.64	0.62
MnO	b.d.l	b.d.l
MgO	b.d.l	b.d.l
CaO	2.73	2.98
Na ₂ O	2.89	3.77
K ₂ O	0.20	0.23
Total	99.37	99.92

b.d.l = below detection limit

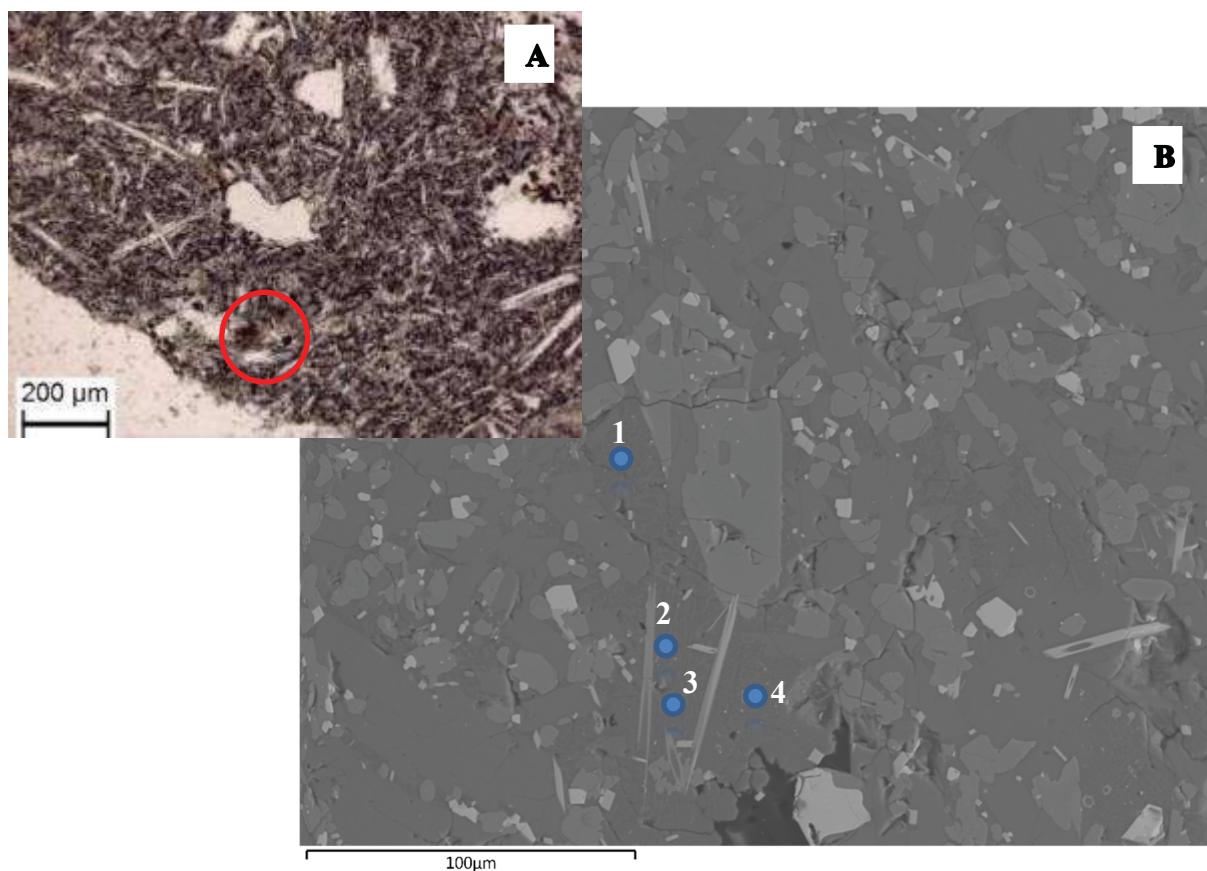


Figure 5.21. Sample HW3. Microphotograph (A) and BSE image (B) and respective points of analysis.

Table 5.8. Sample HW3. EPMA-WDS results concerning the composition of volcanic glass (1-4).

Oxide (%)	1	2	3	4
SiO ₂	61.67	63.76	64.10	63.70
TiO ₂	0.77	0.72	0.65	0.66
Al ₂ O ₃	11.73	11.37	12.00	11.84
Fe ₂ O ₃	0.71	1.04	0.68	0.74
MnO	b.d.l	b.d.l	b.d.l	b.d.l
MgO	0.06	0.10	b.d.l	b.d.l
CaO	1.04	3.43	2.75	2.75
Na ₂ O	1.21	3.42	4.25	4.11
K ₂ O	6.15	0.18	0.31	0.30
Total	83.84	84.25	84.86	84.23

b.d.l = below detection limit

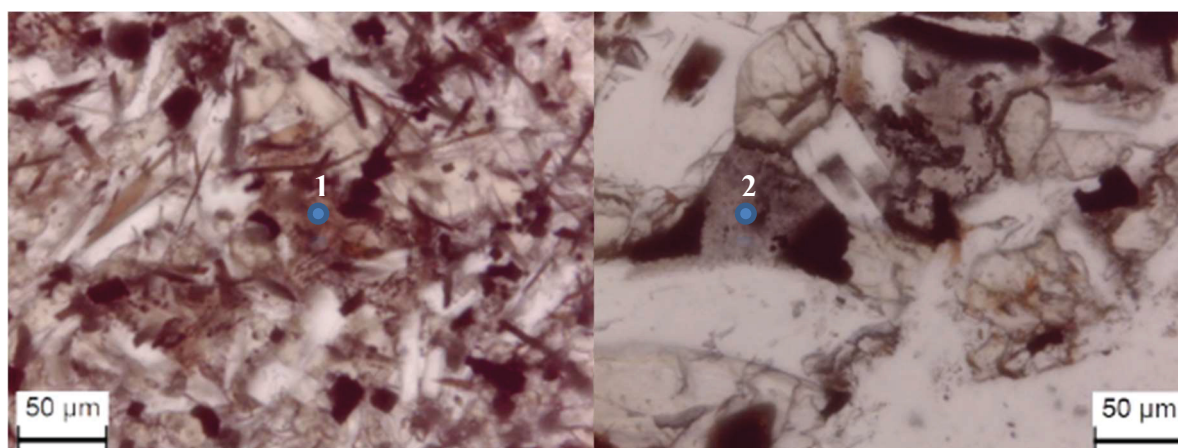


Figure 5.22. Sample HW5. Interstitial brownish volcanic glass and respective examination points for the composition of the volcanic glass.

Table 5.9. Sample HW5. EPMA-WDS results concerning the composition of volcanic glass (1 and 2, Figure 5.22).

Oxides (%)	1	2
SiO ₂	76.93	79.73
TiO ₂	0.61	0.49
Al ₂ O ₃	13.87	12.32
FeO	0.77	0.60
MnO	b.d.l.	b.d.l.
MgO	b.d.l.	b.d.l.
CaO	3.11	2.30
Na ₂ O	4.15	3.89
K ₂ O	0.21	0.25
Total	99.59	99.57
b.d.l = below detection limit		

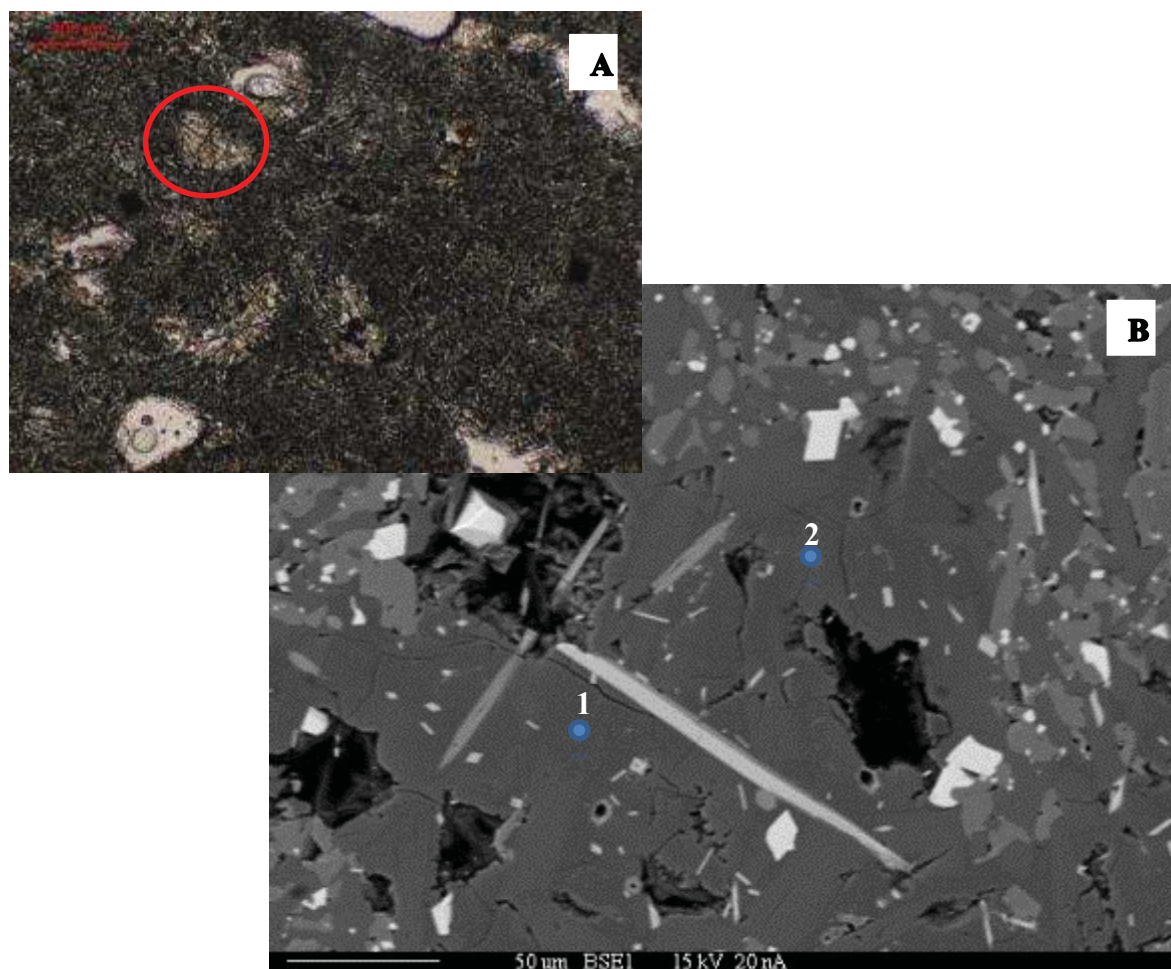


Figure 5.23. Sample HW6. Microphotograph (A), BSE image (B) and points of analysis of interstitial volcanic glass.

Table 5.10. Sample HW6. EPMA-WDS results of the analysis of interstitial volcanic glass (1 and 2, Figure 5.23).

Oxides (%)	1	2
SiO ₂	77.37	77.95
TiO ₂	0.83	1.04
Al ₂ O ₃	12.10	11.45
FeO	1.73	1.45
MnO	b.d.l.	b.d.l.
MgO	0.24	0.23
CaO	1.80	2.27
Na ₂ O	4.44	4.03
K ₂ O	0.81	0.42
Total	99.31	98.84

b.d.l = below detection limit

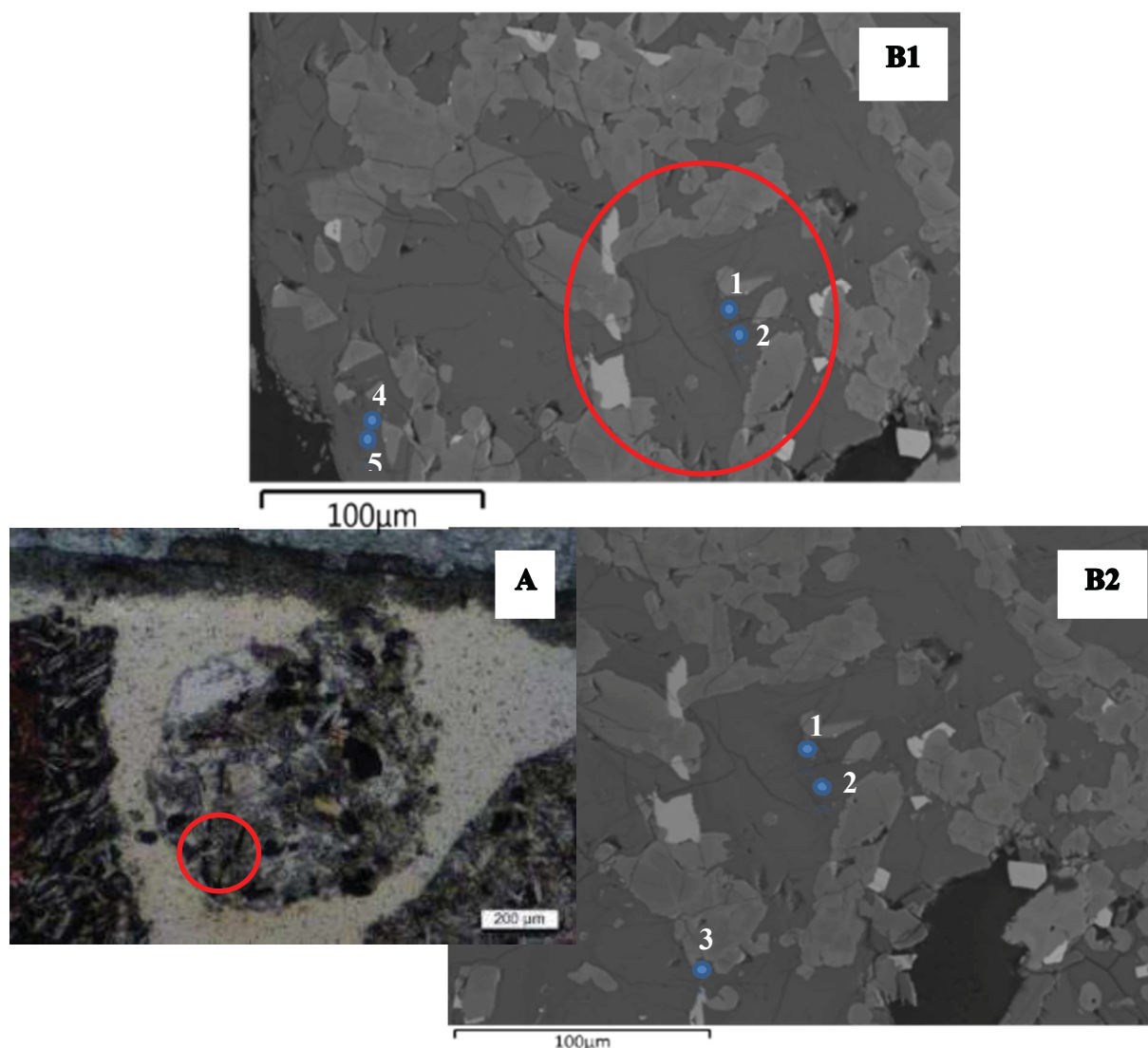


Figure 5.24. Sample HW7. Microphotograph (A), BSE images (B1 and B2) and respective points of analysis. Image B2 corresponds to an amplification of the area in the red circle

Table 5.11. Sample HW7. EPMA-WDS results concerning volcanic glass (1-5).

Oxides (%)	1	2	3	4	5
SiO ₂	76.07	79.98	71.84	76.58	69.84
TiO ₂	0.65	0.98	0.83	0.79	0.17
Al ₂ O ₃	9.71	10.14	10.35	11.08	18.12
FeO	3.69	1.26	0.97	0.67	0.92
MnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MgO	b.d.l.	0.11	b.d.l.	b.d.l.	0.08
CaO	2.04	1.27	5.27	0.38	5.18
Na ₂ O	1.87	3.26	3.45	0.79	3.76
K ₂ O	0.44	0.89	1.57	4.87	0.46
Total	94.73	98.10	94.58	95.38	99.07

b.d.l = below detection limit

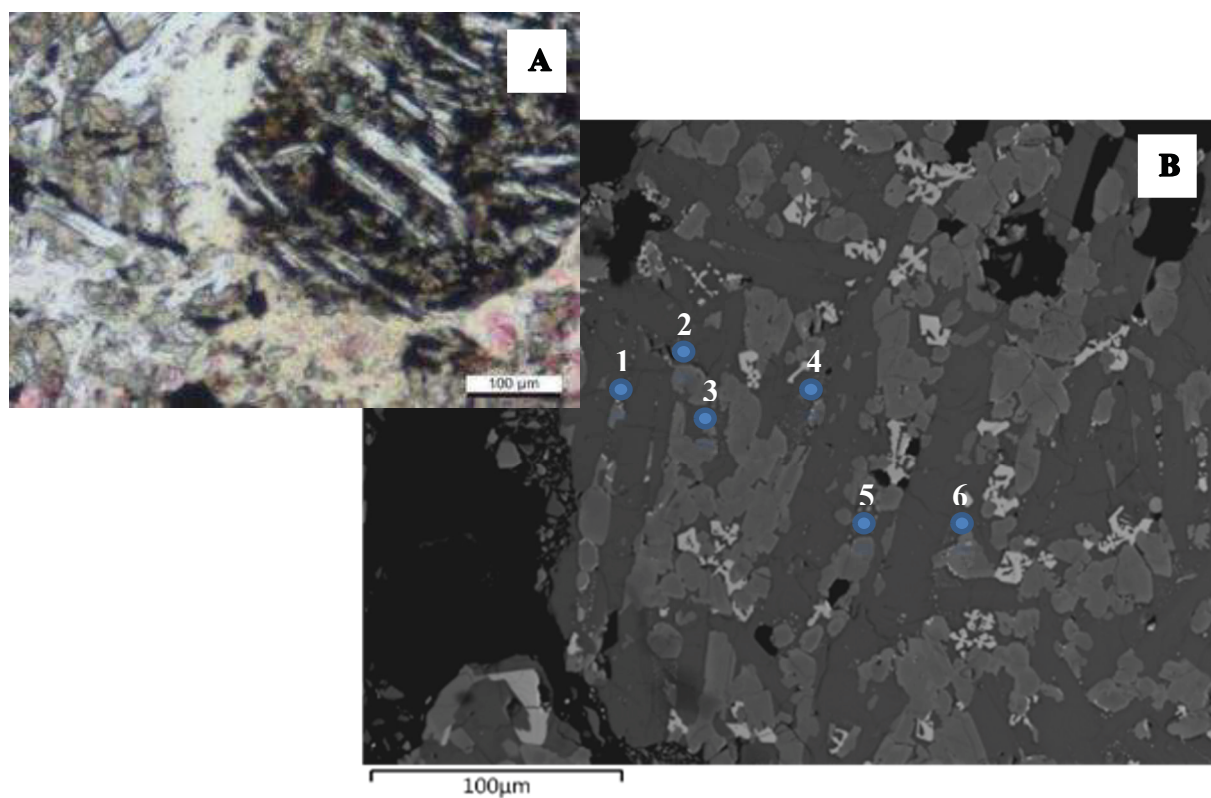


Figure 5.25. Sample HW7. Microphotograph (A), BSE image (B) and respective points of analysis.

Table 5.12. Sample HW7. EPMA-WDS results concerning volcanic glass (1-6).

Oxides (%)	1	2	3	4	5	6
SiO ₂	69.26	67.12	79.7	69.14	69.48	61.81
TiO ₂	2.52	1.89	3.13	1.67	1.92	1.19
Al ₂ O ₃	11.34	11.48	9.94	12.44	10.94	10.66
FeO	5.94	2.89	5.26	5.09	3.73	6.65
MnO	0.10	0.06	0.09	0.10	b.d.l.	0.13
MgO	0.37	0.14	0.33	0.32	0.38	0.44
CaO	3.30	2.92	3.62	6.59	2.22	6.97
Na ₂ O	2.12	1.92	2.30	2.37	1.15	1.74
K ₂ O	1.73	3.09	2.25	1.75	2.88	2.82
Total	96.88	91.76	95.88	96.66	93.01	92.51

b.d.l = below detection limit

Iceland

From the macroscopy point of view, three of the aggregate samples correspond to gravel showing rounded particles of low sphericity (ICL1, ICL2 and ICL4) (Figure 5.26). They contain different rock types (mainly of basaltic composition) and exhibit different colours, from dark grey (some are glossy – ICL4), almost black, and also greenish, reddish and lighter coloured grains. Some of the particles show white/green small crystals, others contain vesicles with secondary minerals and others are highly vesicular. In two of the aggregate samples (ICL2 and ICL4), a group of particles shows sub-angular to sub-rounded shapes. They are massive to vesicular.

The other aggregate sample is a crushed rock (ICL3). The crushed rock forms mainly subangular particles, and some are elongated. All aggregate samples were separated into fractions (F) based on texture and colour. Most of the aggregates are grouped into four fractions containing different lithologies.

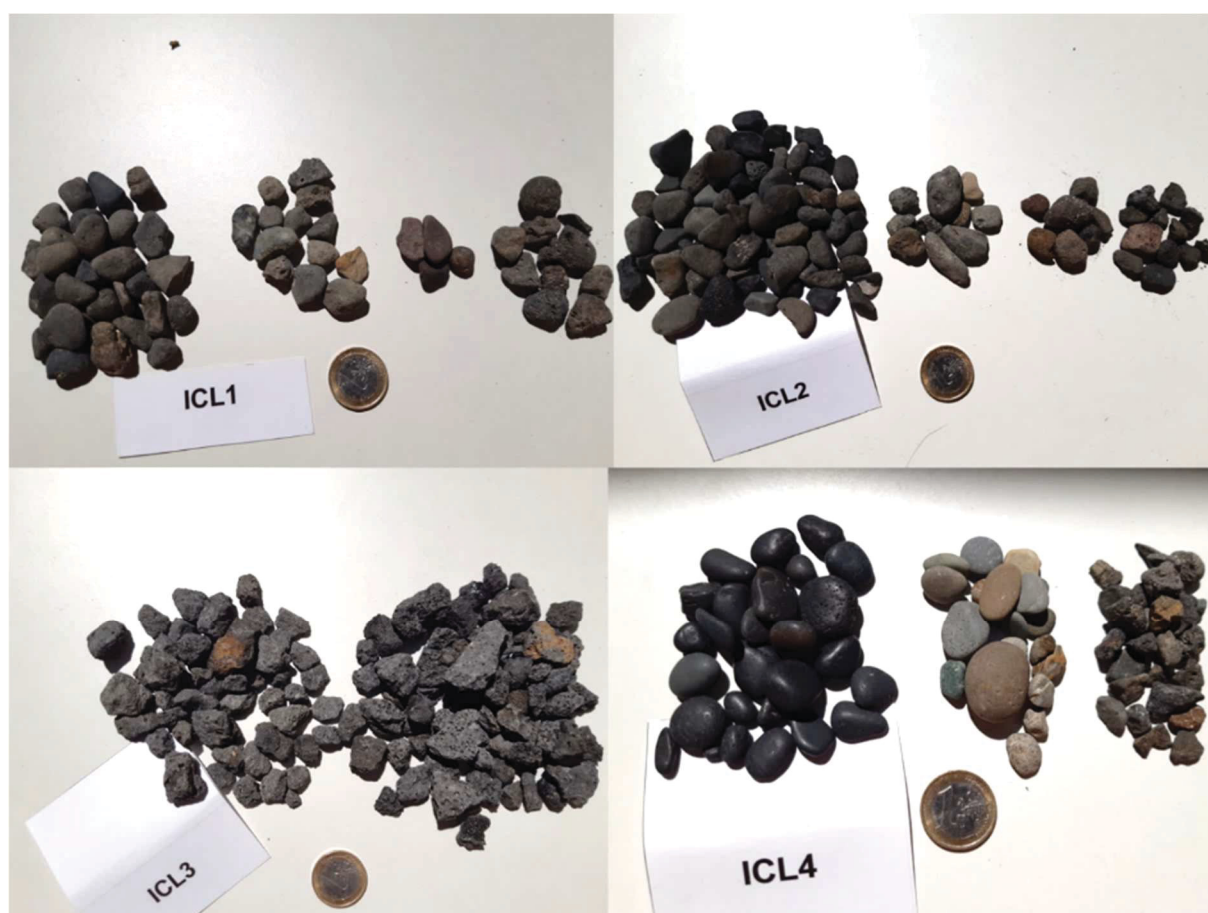


Figure 5.26. Icelandic aggregates are divided into fractions based on the texture and the colour of the particles.

The petrographic analysis of the aggregates from Iceland shows that there are variable lithologies. Those that were collected as gravel (ICL1, ICL2 and ICL4) are constituted by a mix of rock fragments from different origins, mainly of basic composition, and also contain shells. The different fragments of rocks in the gravel correspond to basalt, metabasalt, some rhyolite, dacite and a plutonic rock similar to gabbro. There are also several aggregate particles in the gravel samples that are heavily altered which makes the classification of the original rock a challenge.

In the samples there are basalts with different degrees of alteration (ICL1, ICL2, ICL4), where some of them are classified as metabasalt (ICL1, ICL2); there is also dacite (ICL1), rhyolite (ICL1, ICL2) and rock similar to gabbro (ICL4). The ICL3 sample is different from the others because it is crushed basalt from a quarry.

Basalt, metabasalt, dacite and rhyolite are some of the aggregate particles that compose the gravel sample ICL1. The basaltic aggregate particles show different degrees of alteration and features. Variolitic texture (Figure 5.27A) was observed, displaying skeletal plagioclase laths with fans of dendritic clinopyroxene and small phenocrysts of olivine. Other particles show phenocrysts and microphenocrysts of plagioclase and clinopyroxene (e.g. augite) set in a fine-grained groundmass of the same mineral phases and iddingsite and opaque minerals (titanomagnetite), sometimes in skeletal textures. The phenocrysts of olivine have been completely altered into iddingsite retaining the original habit of the crystal. Sometimes olivine forms glomeroporphyritic clusters either with plagioclase or with plagioclase and clinopyroxene. The plagioclase occurs in euhedral to subhedral crystals, forming frequently glomeroporphyritic clusters with clinopyroxene or with clinopyroxene and iddingsite, replacing olivine, and occasionally appearing zoned. The clinopyroxene also shows euhedral to subhedral crystals mostly with undulose extinction. Clay minerals are scattered irregularly in the basaltic fragment. Other basaltic aggregate particles present the same mineral assemblage and the same features but are more intensely altered. The clinopyroxene crystals also show an undulose extinction and those of plagioclase occur in skeletal laths with sections altered to calcite. Calcite and clay minerals appear irregularly in the fine-grained groundmass given imprinting a brownish colour. In some particles phenocrysts and microphenocrysts of plagioclase form glomeroporphyritic clusters. There are also microphenocrysts of olivine but this mineral has been completely replaced by iddingsite. The groundmass is formed by plagioclase and clinopyroxene. Opaque minerals appear as accessory minerals, sometimes in skeletal forms. The volcanic glass seems altered into a devitrified volcanic glass and is scattered in different areas of the rock (Figure 5.27B).

The fragments of metabasalts show peculiar features where amygdules are filled with zeolites in the centre and chlorite-smectite minerals surrounding them, both rimmed by a thin layer of celadonite (green colour) and sometimes accompanied with silica forms (Figure 5.27C). Other pores seem to contain only smectite. The groundmass of these metabasalts is altered to fine-grained brown minerals that are difficult to identify in thin sections and are referred to simply as clay minerals and/or palagonite. Plagioclase, zeolite and chlorite are visible in the groundmass, the last two seem to fill the interstices of the rock.

Rhyolite particles show darker and lighter areas. The lighter areas are composed of grains of quartz, tridymite (Figure 5.27D), K-feldspar, some yellowish green chlorites, minor plagioclase, traces of pyroxene and opaque minerals. The darker areas correspond to devitrified glass with cryptocrystalline and spherulitic texture (Figure 5.27E). Chlorite crystals fill some of the pores of the rock.

Dacite shows a porphyritic texture containing phenocrysts of plagioclase, quartz and relict crystals of clinopyroxene. Brownish orange clay minerals are scattered all over the rock which seems to result from the alteration of clinopyroxene, still visible in some sections of the rock. Silica is present as tridymite with wedged shape crystals and euhedral quartz (EPMA-WDS and EDS spectra) in the centre of the spherules or the groundmass. The spherules are composed of feldspar and silica minerals confirmed by EPMA-WDS and EDS spectra. Plagioclase (e.g. andesine) presents euhedral to subhedral crystals, some appear zoned and sometimes form glomeroporphyritic clusters either monomineralic or together with relict crystals of clinopyroxene. The plagioclase phenocrysts show cracks that are filled by clay minerals. The opaque minerals are associated with phenocrysts, especially plagioclase. Minor quantities of amphibole are also visible in this rock. The rock also displays brownish areas of devitrified glass confirmed by EPMA with cryptocrystalline texture in the groundmass. Spherulitic textures are also visible in the brownish area. There are also dacite particles with the same mineral assemblage but do not show spherules. The grains of quartz form clusters that are dispersed in several areas of the rock and the plagioclase appears as phenocrysts or microphenocrysts in the cryptocrystalline groundmass. Chlorite surrounds the vesicles.

Other aggregate particles show agglomerations of grains of quartz, altered plagioclase and chlorite. This last one is rimming or filling the vesicles and also is present in the groundmass. The groundmass has a brownish colour probably due to the presence of clay minerals and some parts display microcrystalline quartz.

An aggregate particle resembles the chilled margin from pillow lava, where the margin quenched to yellow volcanic glass and in the more slowly cooled interior brown spherical bodies grew that increased in abundance, coalescing into a solid mass (Figure 5.27F). Some

vesicles are also visible. Different aggregate particles were subjected to further analysis by EPMA to identify some of the components.

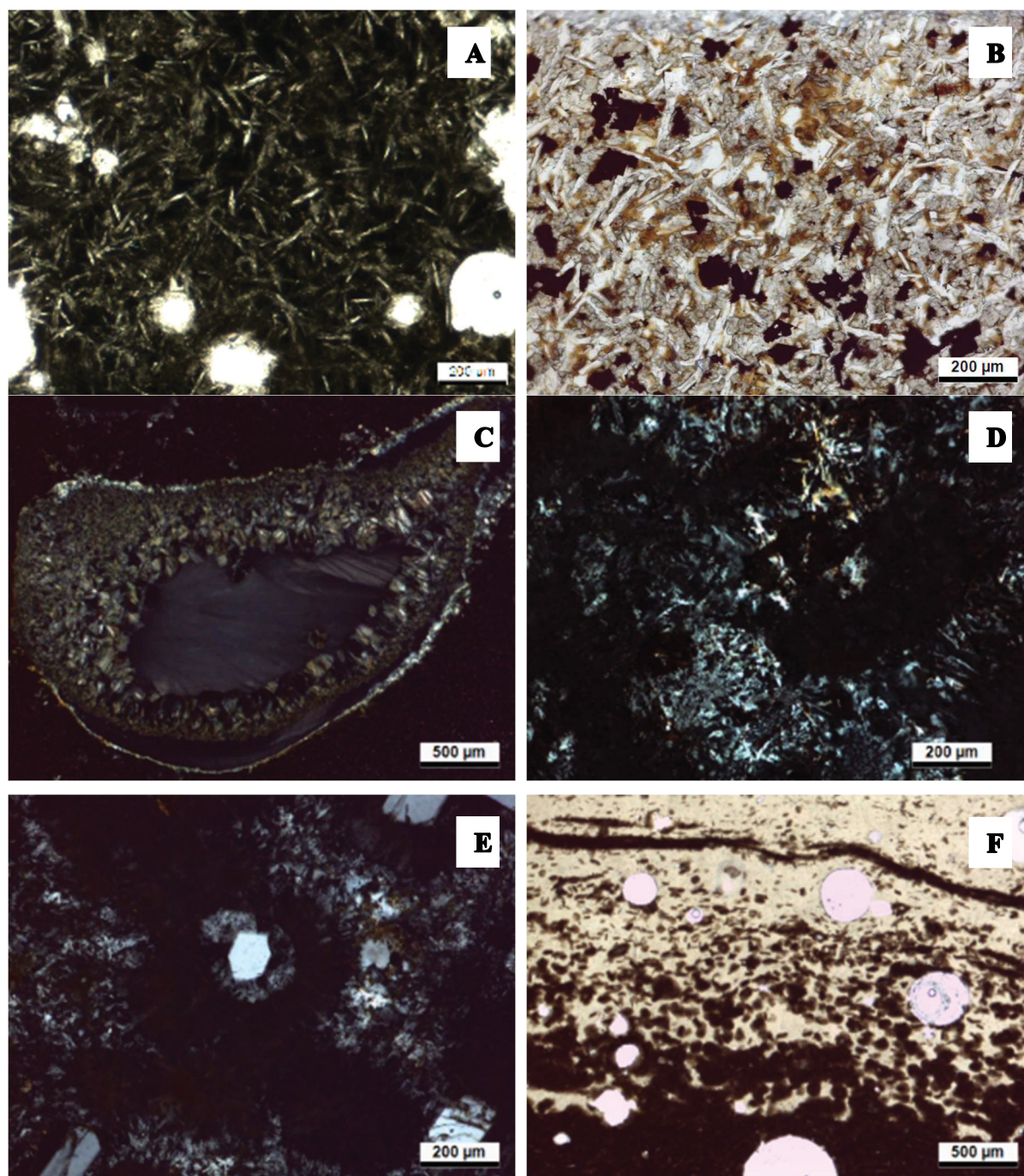


Figure 5.27. Photomicrographs of ICL1 sample: C, D and E in XPL; A, B and F in PPL. A) Variolitic texture; B) Basalt containing altered volcanic glass; C) Pore space with zeolite and chlorite/smectite in a metabasalt; D) Tridymite in rhyolite aggregate particle; E) Dacite with spherulitic texture involving an euhedral crystal of quartz; F) Volcanic glass with brown spherical bodies and pores.

Figure 5.28 shows a volcanic glass in basalt, more devitrified according to the texture observed in the BSE image and with two EDS spectra. Also in ICL1-F1, chlorite-smectite minerals (C/S) and zeolite were identified in a vesicle of a metabasalt, by using EPMA (Figure 5.29 and Table 5.13).

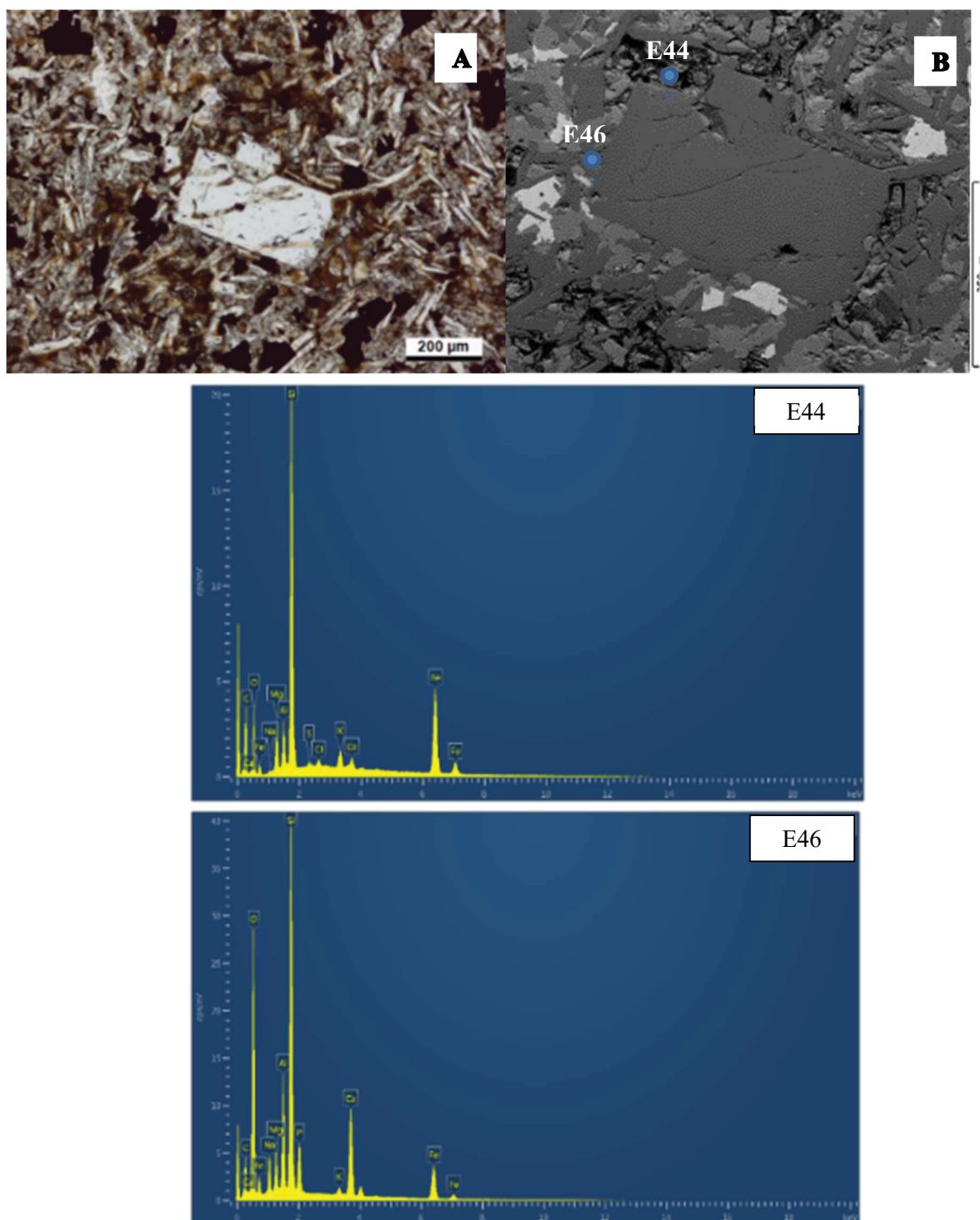


Figure 5.28. Basalt in ICL1-F1 (basalt). Photomicrograph (A), BSE image (B) and respective EDS spectra of volcanic glass (E44 and E46).

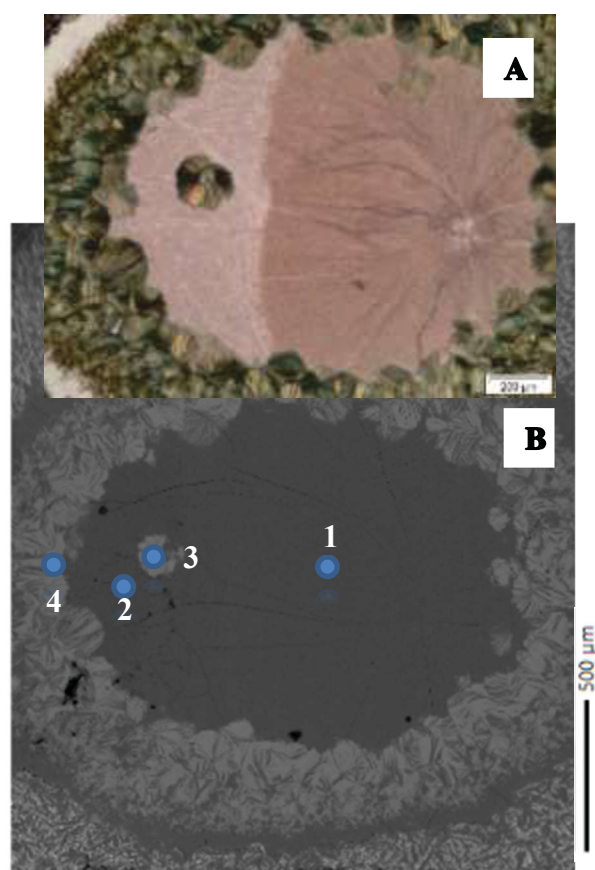


Figure 5.29. Metabasalt in ICL1-F1. Photomicrograph (A) and BSE image (B) and respective points of analysis.

Table 5.13. Sample ICL1-F1. EMPA-WDS results of zeolite (1,2) (indicative) and chlorite (3,4).

Oxides (%)	1	2	3	4
SiO ₂	49.21	49.54	28.53	28.50
TiO ₂	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al ₂ O ₃	26.65	26.95	14.20	14.08
FeO	b.d.l.	b.d.l.	29.29	29.40
MnO	b.d.l.	b.d.l.	b.d.l.	0.15
MgO	b.d.l.	b.d.l.	13.78	13.39
CaO	10.93	10.93	0.88	1.05
Na ₂ O	1.84	1.57	0.11	0.10
K ₂ O	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Total	88.72	89.13	86.79	86.67

b.d.l. = below detection limit

Also in the dacite, BSE images (Figure 5.30A and 5.30C) and EPMA analyses led to the identification of plagioclase, quartz and alkali feldspar forming a spherulitic texture (Figures 5.30C and Tables 5.14 and 5.15). EDS spectra was also obtained for quartz and plagioclase minerals (Figure 5.30C).

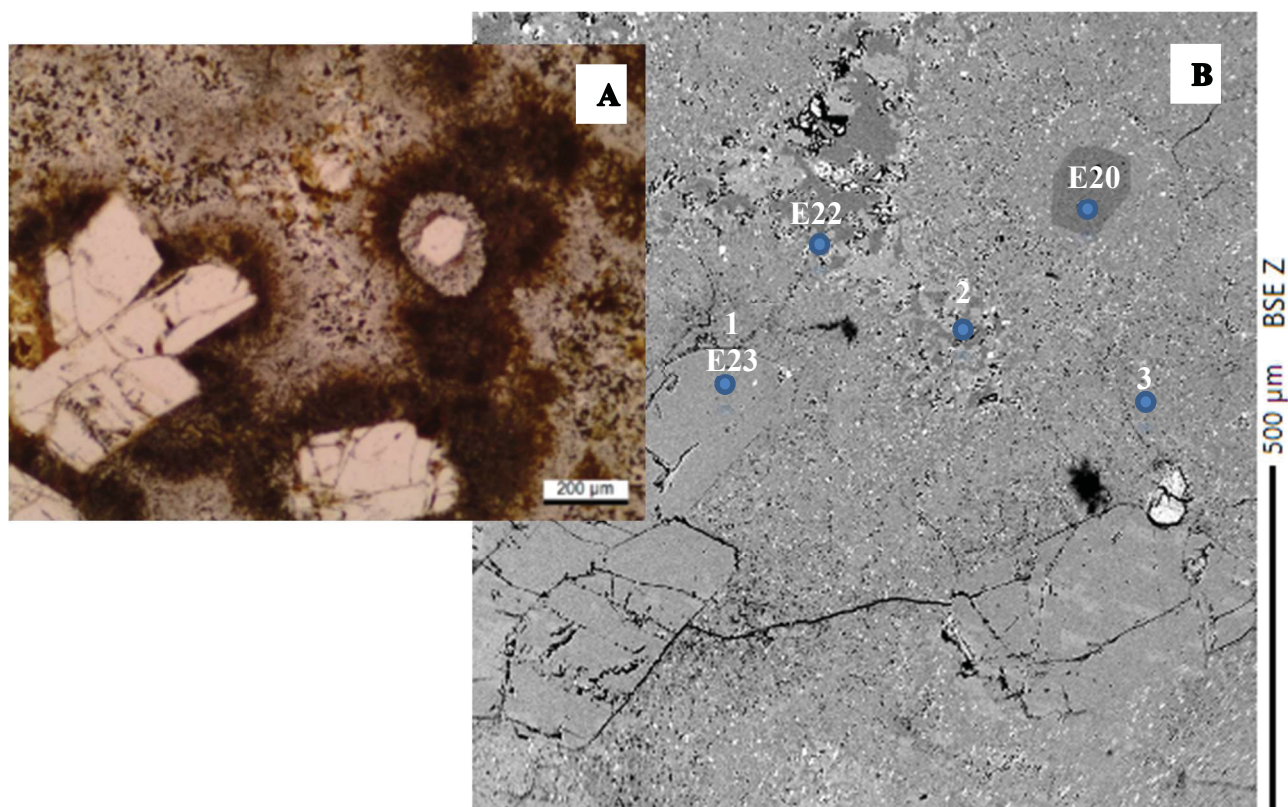


Figure 5.30A. Dacite in ICL1-F2: Photomicrograph (A) and BSE image (B) and respective points of analysis.

Table 5.14. Sample ICL1-F2. EPMA-WDS results of plagioclase (1), quartz (2) and volcanic glass (3) in dacite.

Oxides (%)	1	2	3
SiO ₂	63.81	97.92	68.23
TiO ₂	-	-	0.01
Al ₂ O ₃	22.15	0.50	17.20
FeO	0.23	0.28	0.88
MnO	b.d.l.	-	b.d.l.
MgO	b.d.l.	-	0.12
CaO	3.64	-	0.37
Na ₂ O	8.82	-	6.09
K ₂ O	0.65	-	5.84
Total	99.34	98.73	98.75

b.d.l = below detection limit

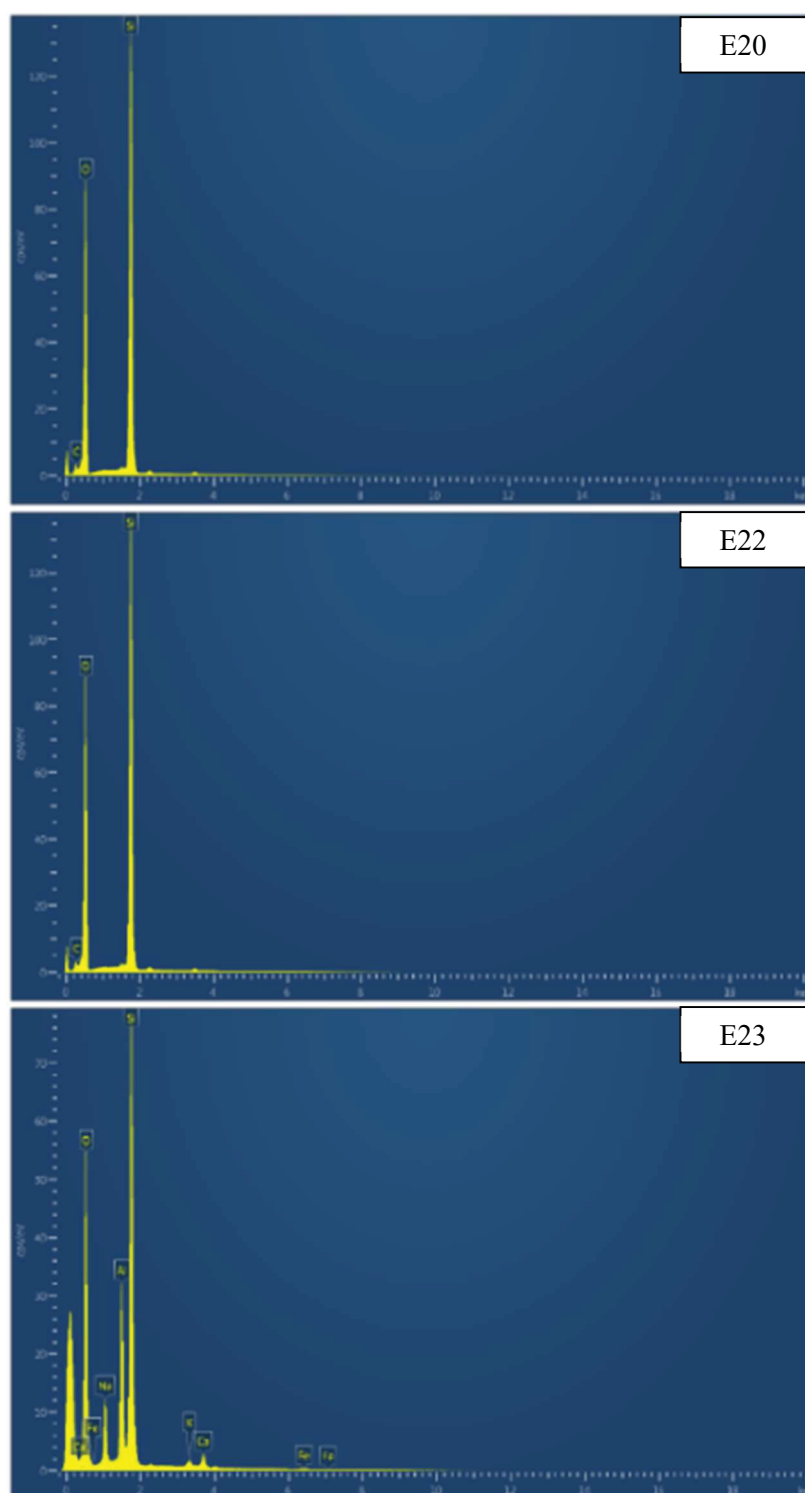


Figure 5.30B. Dacite in ICL1-F2: EDS spectra of quartz (E20 and E22) and plagioclase (E23), in Figure 5.30A.

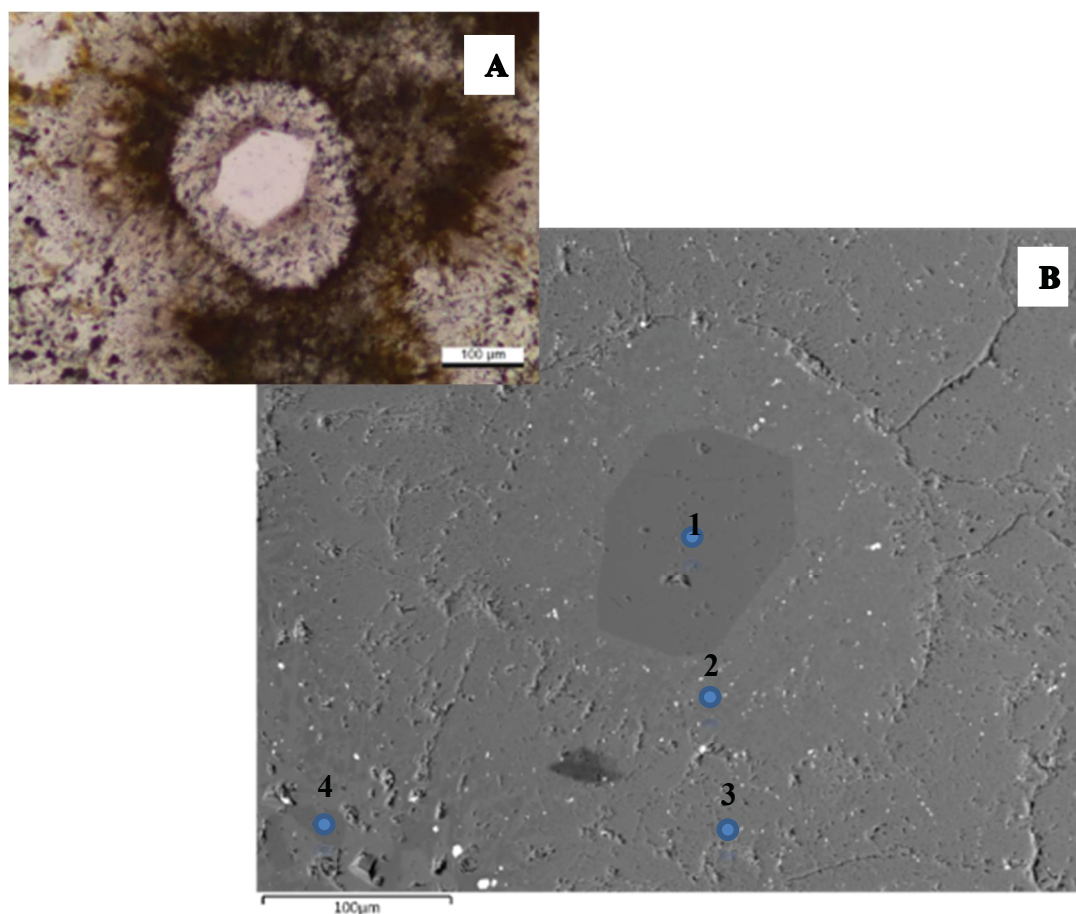


Figure 5.30C. Sample ICL1-F2 (Dacite). Microphotograph (A) and BSE image (B) (a detail of Figure 5.30A) with the points of analysis.

Table 5.15. Sample ICL1-F2. EPMA-WDS results of quartz (1 and 4) and alkali feldspar (2 and 3).

Oxides (%)	1	2	3	4
SiO ₂	98.73	73.35	75.06	97.92
TiO ₂	-	0.10	-	-
Al ₂ O ₃	-	15.02	13.01	-
FeO	-	0.81	0.50	-
MnO	-	-	-	-
MgO	-	0.05	-	-
CaO	-	0.50	0.30	-
Na ₂ O	-	6.26	4.96	-
K ₂ O	-	3.96	3.61	-
Total	98.78	100.10	97.50	98.99

In ICL1-F3, a rhyolite aggregate particle was also analysed by EPMA where quartz and feldspar were confirmed in the groundmass (Figure 5.31 and Table 5.16).

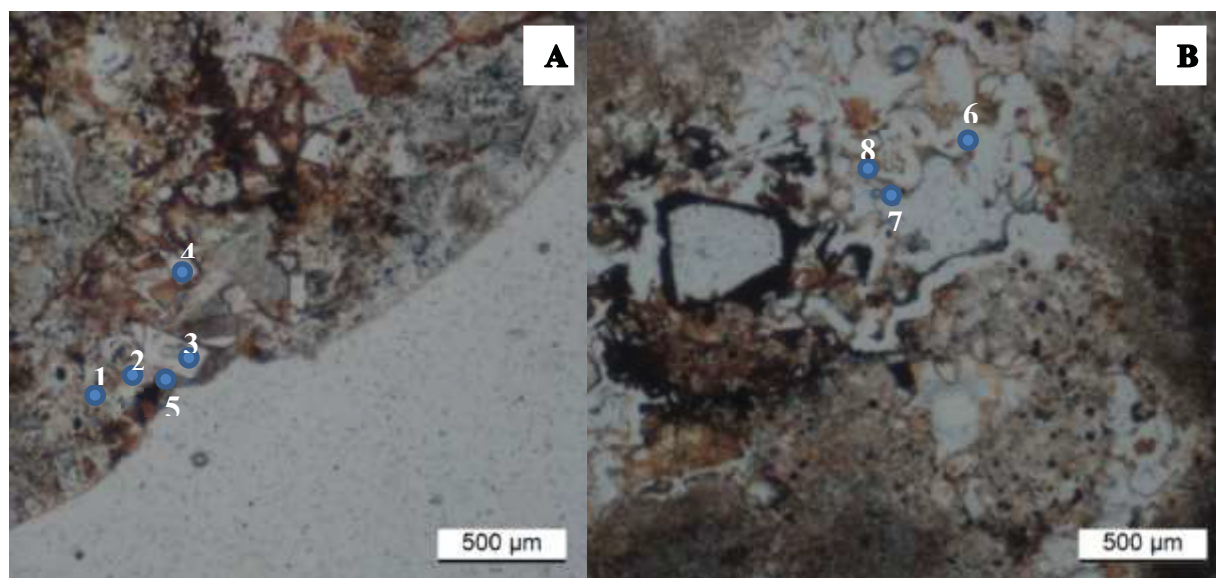


Figure 5.31. Rhyolite in ICL1-F3: A) Image with the points of analysis 1 to 5 and B) Image with the points of analysis 6 to 8.

Table 5.16. Sample ICL1-F3. EMPA-WDS results of quartz (1, 2, 5, 6, 7 and 8,) and alkali feldspar (3 and

Oxides (%)	1	2	3	4)	5	6	7	8
SiO ₂	97.40	97.11	66.90	66.80	96.95	97.52	97.99	97.94
TiO ₂	-	-	-	-	-	-	-	-
Al ₂ O ₃	0.64	0.65	18.35	18.02	0.66	0.60	0.35	0.58
FeO	-	-	0.31	0.33	-	-	-	-
MnO	-	-	-	-	-	-	-	-
MgO	-	-	-	-	-	-	-	-
CaO	-	-	-	0.09	-	-	-	-
Na ₂ O	0.12	0.19	5.85	5.89	0.15	-	-	-
K ₂ O	-	-	8.32	8.12	-	-	-	-
Total	98.43	98.22	99.79	99.30	98.16	98.41	98.54	98.69

In the fraction ICL1-F4, analyses were also performed in a metabasalt particle aiming at identifying zeolite filling a vesicle, and chlorite-smectite minerals filling a gap in one of the zeolite crystals (Figure 5.32 A and B).

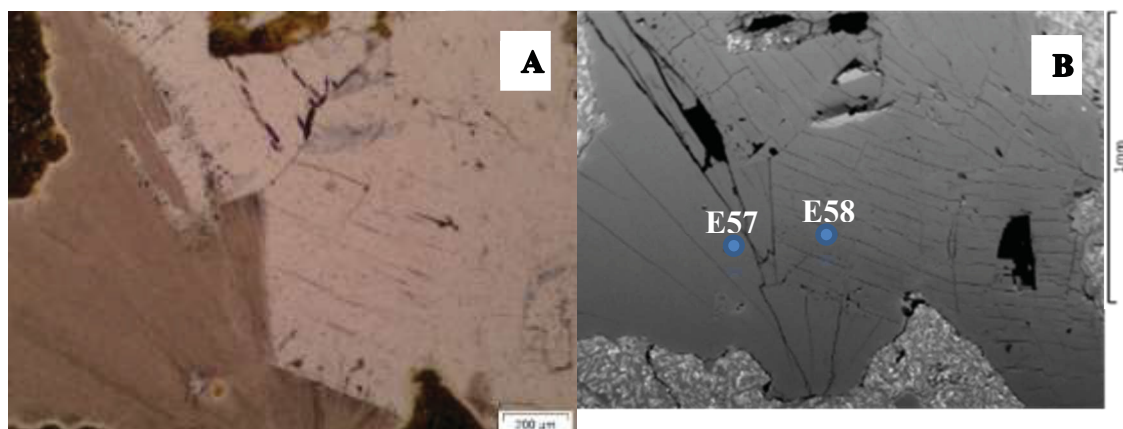


Figure 5.32A. Metabasalt in ICL1-F4: Photomicrographs (A) and BSE image (B) indicating the points of analysis.

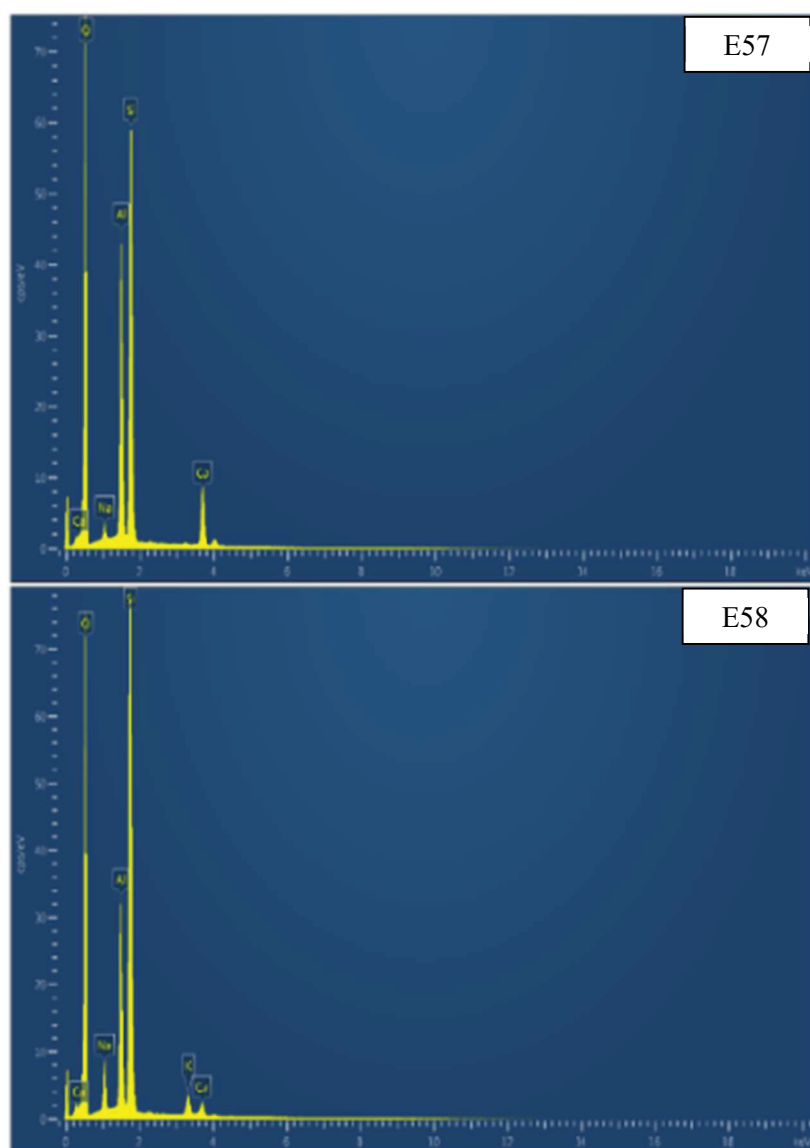


Figure 5.32B. Metabasalt in ICL1-F4: EDS spectra of zeolites (E57 and E58).

The gravel that constitutes the ICL2 sample has fragments of particles mainly of basalt, metabasalt and rhyolite.

The basalt shows subophitic and porphyritic textures and presents different degrees of alteration. In the subophitic texture, plagioclase crystals enclose clinopyroxene crystals. In the majority of the basaltic particles, olivine has been replaced by iddingsite; devitrified volcanic glass is scattered across the rock (Figure 5.33A) and palagonite, an isotropic orange material, seems to be replacing olivine. In some sections, calcite occurs dispersed in the devitrified volcanic glass. In other cases, chlorite is the mineral that is dispersed in the rock (Figure 5.33B). In one of the fragments, the plagioclase crystals show some degree of alteration and very few vesicles are partially filled with zeolites and chlorite. In others, there are large euhedral phenocrysts of olivine (Figure 5.33C), some reaching 2 mm in width. The smaller crystals form glomeroporphyritic clusters with plagioclase. Also, olivine shows embayments and skeletal textures. Plagioclase also forms monomineralic glomeroporphyritic clusters and is widely present in the groundmass. The groundmass displays peculiar features of brownish and lighter areas (Figure 5.33D); it seems that it cooled down very fast forming some kind of variolitic texture containing fans of dendritic clinopyroxene. EDS and EPMA analyses were performed to identify yellowish volcanic glass with some degree of alteration occurring in the matrix.

The metabasalt shows fine-grained groundmass containing plagioclase, clinopyroxene and opaque minerals. A brownish clay mineral is scattered all over the rock of one of the metabasalt particles. Olivine crystals are altered to iddingsite. Zeolite, which occurs in agglomerates of crystals with a low birefringence, in the BSE image displays a lamellar habit, similar to clay. When vesicles are present and are filled, the centre contains zeolites, which are rimmed by chlorite and chlorite-smectite minerals and silica. The plagioclase crystals are cracked and seem to be suffering some alteration (Figure 5.33E) with zeolite and chlorite filling the cracks. The rhyolite (Figure 5.33F) particles have the same mineralogy and texture as the ones described in ICL1.

Palagonite observed in the BSE image (Figure 5.34A) was identified in the basalt present in ICL2-F1, by EDS (Figure 5.34B) which under an optical microscope occurs as an isotropic material.

A yellowish material was observed in the fraction ICL2-F2. It is not completely isotropic under crossed polarized and it is dispersed throughout the matrix of the rock with some degree of alteration. EPMA analyses were carried out to know the composition of this material that is adjacent to a crystal of plagioclase (Figure 5.35 and Table 5.17).

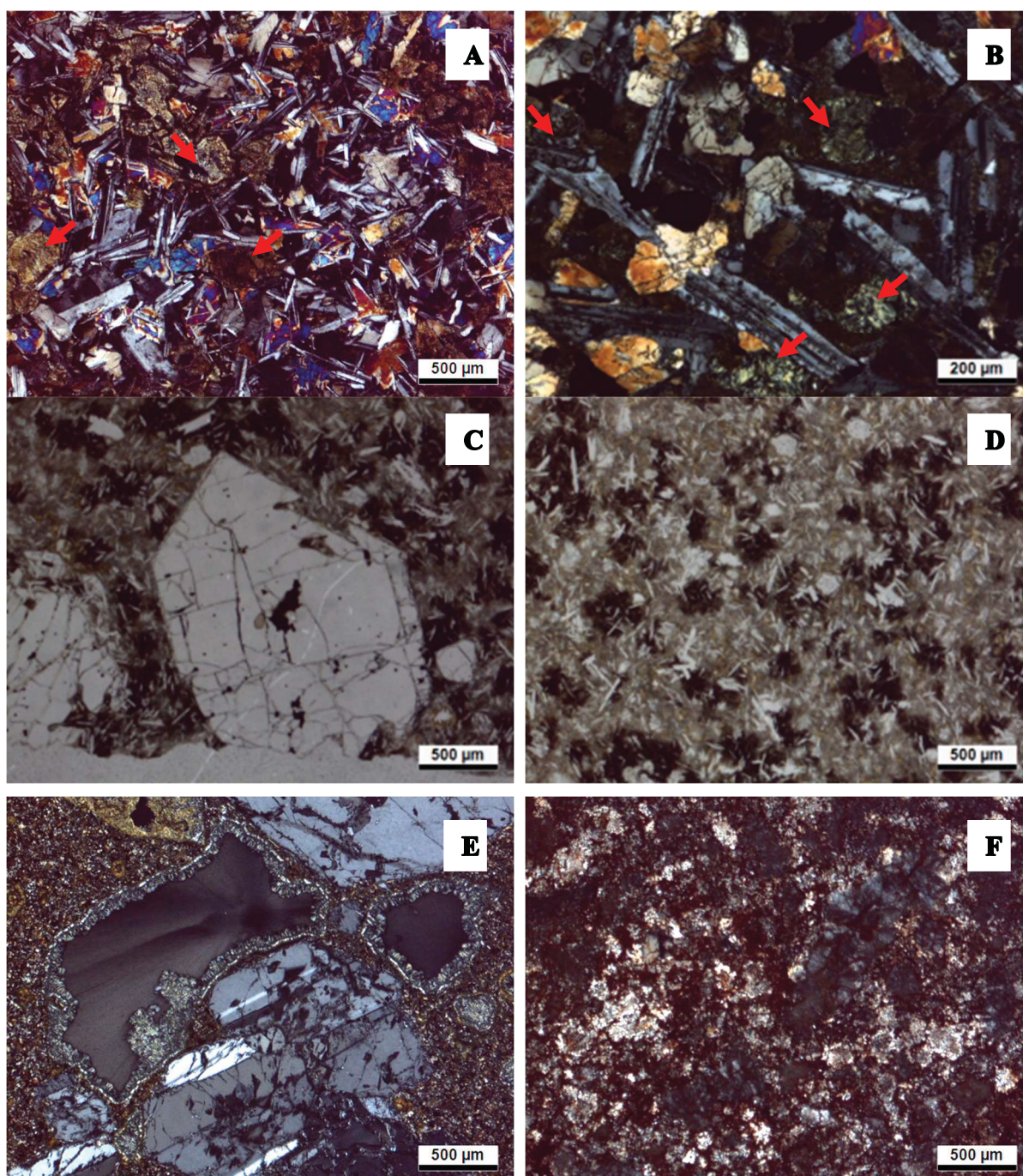


Figure 5.33. Photomicrographs of ICL2 sample: A, B, E and F in XPL; C and D in PPL. The red arrows point to the devitrified glass material in A) and chlorite in B). A) Basalt with subophitic texture and scattered devitrified glass; B) Basalt with subophitic texture and scattered chlorite; C) Large euhedral olivine phenocryst in basalt; D) Basalt with a peculiar texture containing fans of dendritic clinopyroxene; E) Metabasalt with cracked plagioclase and a vesicle filled with zeolite, in the nucleus, and chlorite at the rim; F) Rhyolite aggregate particle.

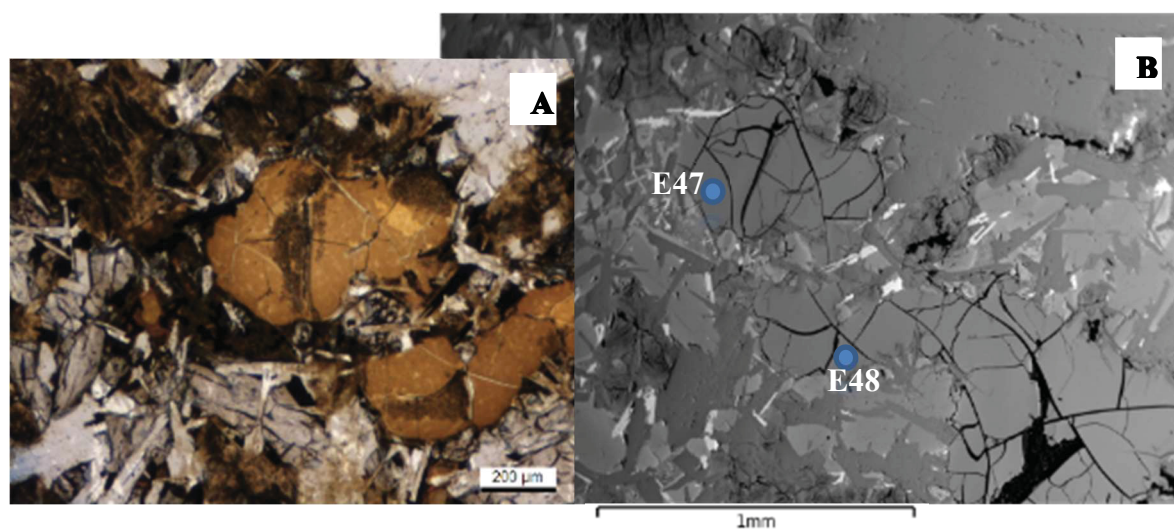


Figure 5.34A. Sample ICL2-F1 (metabasalt). Photomicrographs (A) and BSE images (B) and respective points of analysis.

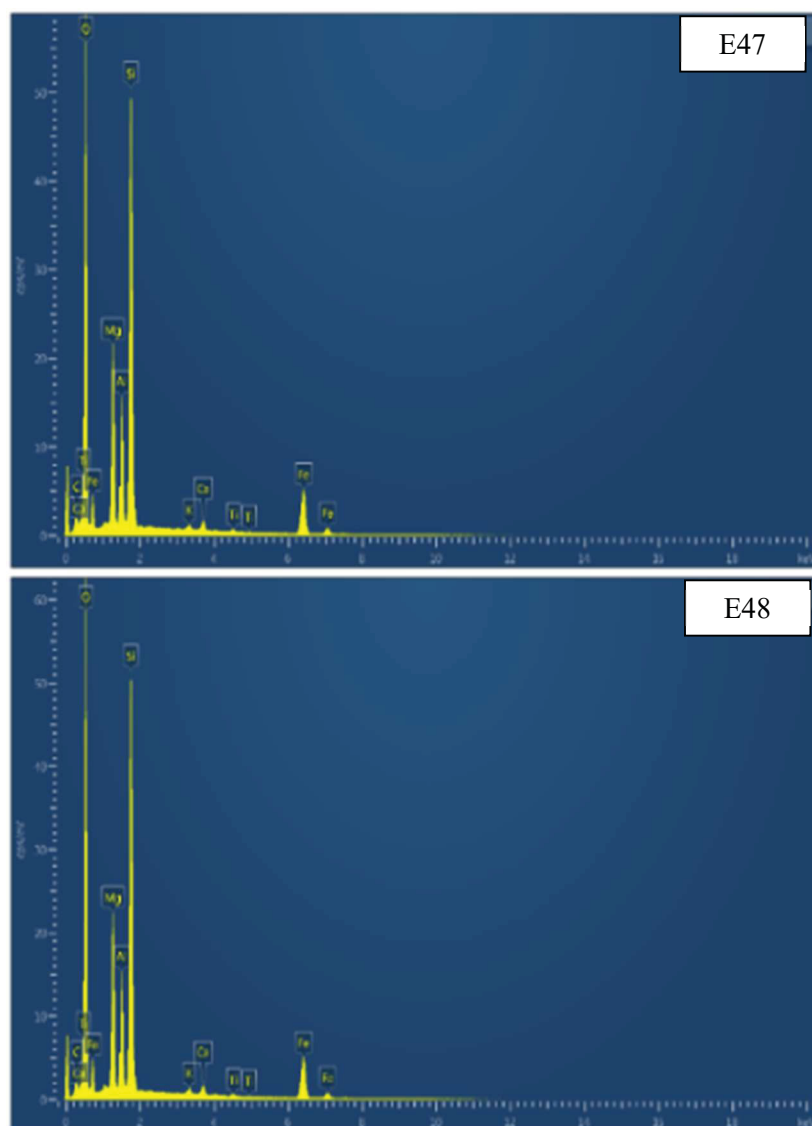


Figure 5.34B. EDS spectra of volcanic glass (E47 and E48).

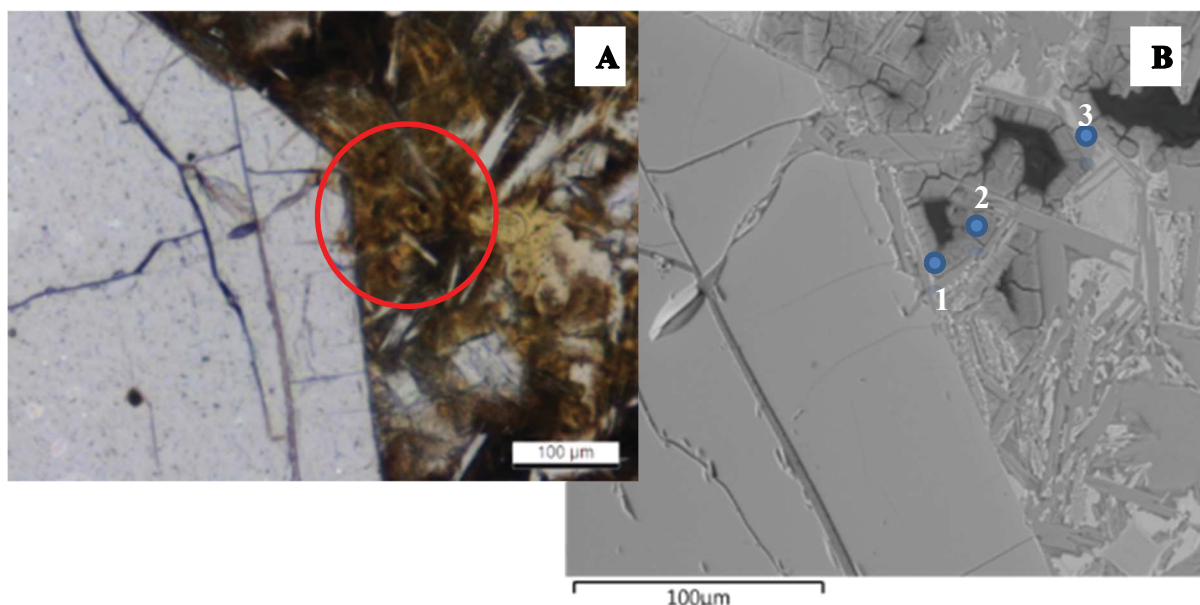


Figure 5.35. Sample ICL2-F2 (Basalt). Photomicrographs (A) and BSE images (B) and respective points of analysis.

Table 5.17. Sample ICL2-F2 EMPA-WDS results of the yellowish material (1, 2 and 3).

Oxides (%)	1	2	3
SiO ₂	46.35	51.16	45.75
TiO ₂	0.37	0.05	2.34
Al ₂ O ₃	4.61	2.81	8.01
FeO	15.50	14.11	16.71
MnO	0.25	0.19	0.25
MgO	18.52	18.33	8.70
CaO	1.88	0.46	14.76
Na ₂ O	0.83	0.42	0.33
K ₂ O	0.69	0.62	0.15
Total	89.92	88.33	97.13

The rock that forms the ICL3 sample is porphyritic with phenocrysts of plagioclase (up to 1 mm) (Figure 5.36A), clinopyroxene (augite) and olivine. The groundmass contains the same mineral assemblage and opaque minerals. The aggregate particles frequently display subophitic (Figure 5.36B), variolitic (Figure 5.36C), and vesicular textures (Figure 5.36D). In the variolitic texture, the clinopyroxene shows dendritic forms between the plagioclase laths. The minerals are euhedral to subhedral and form glomeroporphyritic clusters either of plagioclase (Figure 5.36E) or together with olivine or augite. In the groundmass, the plagioclase crystals show skeletal laths and the phenocrysts are sometimes zoned. The olivine displays also skeletal textures (Figure 5.36F) and embayments. This rock contains very rare volcanic glass.

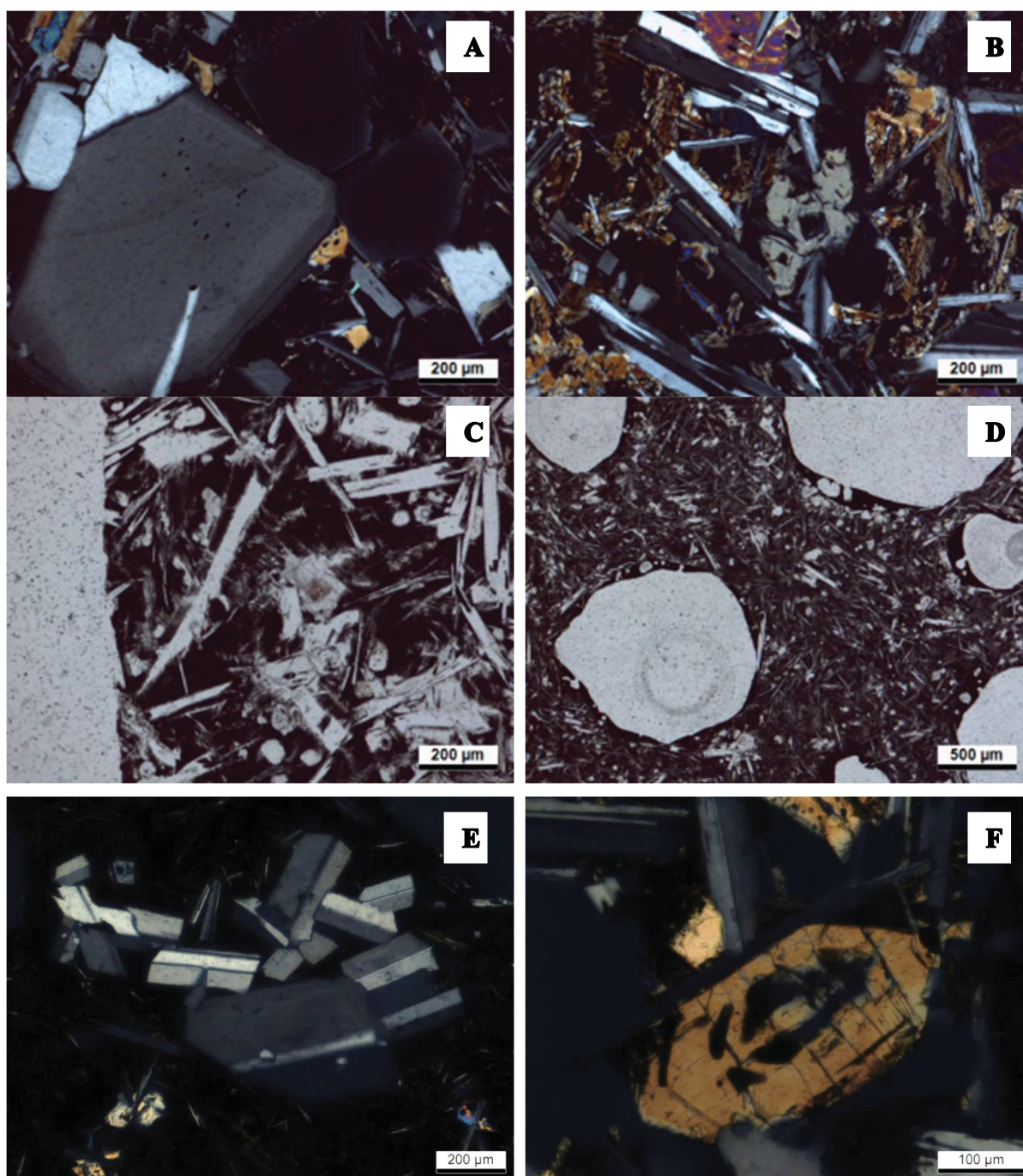


Figure 5.36. Photomicrographs of ICL3 sample: A, B, E and F in XPL; C and D in PPL. A) Plagioclase phenocryst; B) Basalt with subophitic texture; C) Basalt with variolitic texture; D) Vesicular texture; E) Glomeroporphyritic clusters of plagioclase; F) Skeletal crystal of olivine.

The ICL4 sample contains basalts, a rock resembling a hydrothermal rock and a rock similar to gabbro.

The basalt is high to poorly porphyritic with phenocrysts and microphenocrysts mainly plagioclase and olivine and clinopyroxene. In some of the aggregate particles, the phenocrysts are set in a very fine-grained groundmass, and in one of the particles, the rock is banded lava with darker and lighter areas (Figure 5.37A) that owns this aspect probably to the oxygen fugacity. Other phenocrysts are set in a dark basaltic glass (tachylite) groundmass (Figure 5.37B). The olivine crystals show embayments and skeletal textures and form glomeroporphyritic clusters with plagioclase. Other basaltic aggregate particles contain phenocrysts of plagioclase and clinopyroxene forming glomeroporphyritic clusters but they are set in a groundmass formed by feathery clinopyroxene and skeletal plagioclase (Figure 5.37C).

There is a glassy basaltic particle mainly with plagioclase and clinopyroxene and minor olivine (Figure 5.37D). In various areas of the aggregate particle, the first two minerals are forming glomeroporphyritic clusters. The plagioclase displays skeletal textures. Occasionally, opaque minerals occur. A part of the glass is starting to alter into a more brownish colour. Also, in some areas, a yellowish-green material occurs and it was identified by EPMA as volcanic glass.

The rock that resembles a hydrothermally originated rock is formed by altered plagioclase either as phenocryst or in the groundmass. Calcite is also present and it is distributed in some sections of the matrix. Pyrite appears in square crystals. Green needles of a mineral are scattered throughout the matrix, but the identification was not possible at this scale. Figure 5.37E shows crystals of plagioclase and pyrite.

The coarse-grained rock similar to gabbro is mainly formed by plagioclase and clinopyroxene, also containing chlorite and abundant opaque minerals. Overall, this rock has some degree of alteration, with all minerals suffering alteration (Figure 5.37F).

Some features of the minerals and mineraloids were further analysed with the help of EPMA-WDS and EDS. The EDS analysis of the aggregate particle with hydrothermal alteration showed the occurrence of pyrite (Figure 5.38). Also in basalt, an orange brownish material, isotropic to slightly or complete anisotropic, shows some degrees of crystallization (AGSI, AGSII, Stroncik and Schmincke, 2007). The chemical composition indicates that it may be palagonite (Figure 5.39 and Table 5.18). In the glassy basalt particle, the presence of volcanic glass is confirmed by the images and analyses (Figures 5.40, 5.41 and Tables 5.19, 5.20). Also, in Figure 5.40 and the EPMA-WDS analysis given in Table 5.19, seem to point out to the presence of smectite minerals.

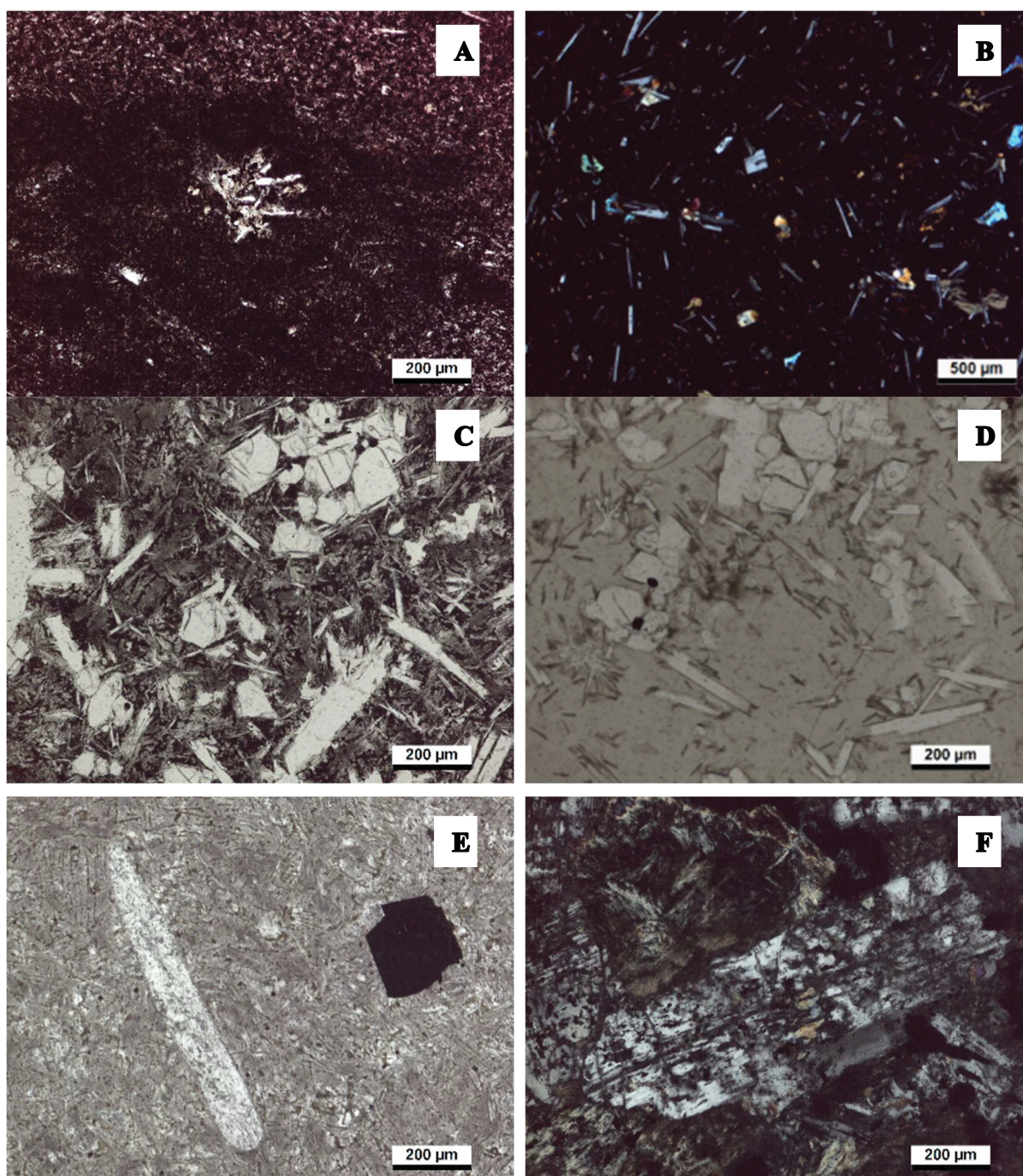


Figure 5.37. Photomicrographs of ICL4 sample: B in XPL; A, C, D, E and F in PPL. A) Banded lava; B) Tachylite groundmass in a Basalt particle; C) Feathery clinopyroxene in a basaltic particle; D) Glassy basalt; E) Prismatic plagioclase lath and pyrite crystal; F) Altered plagioclase in a coarse-grained particle (similar to gabbro).

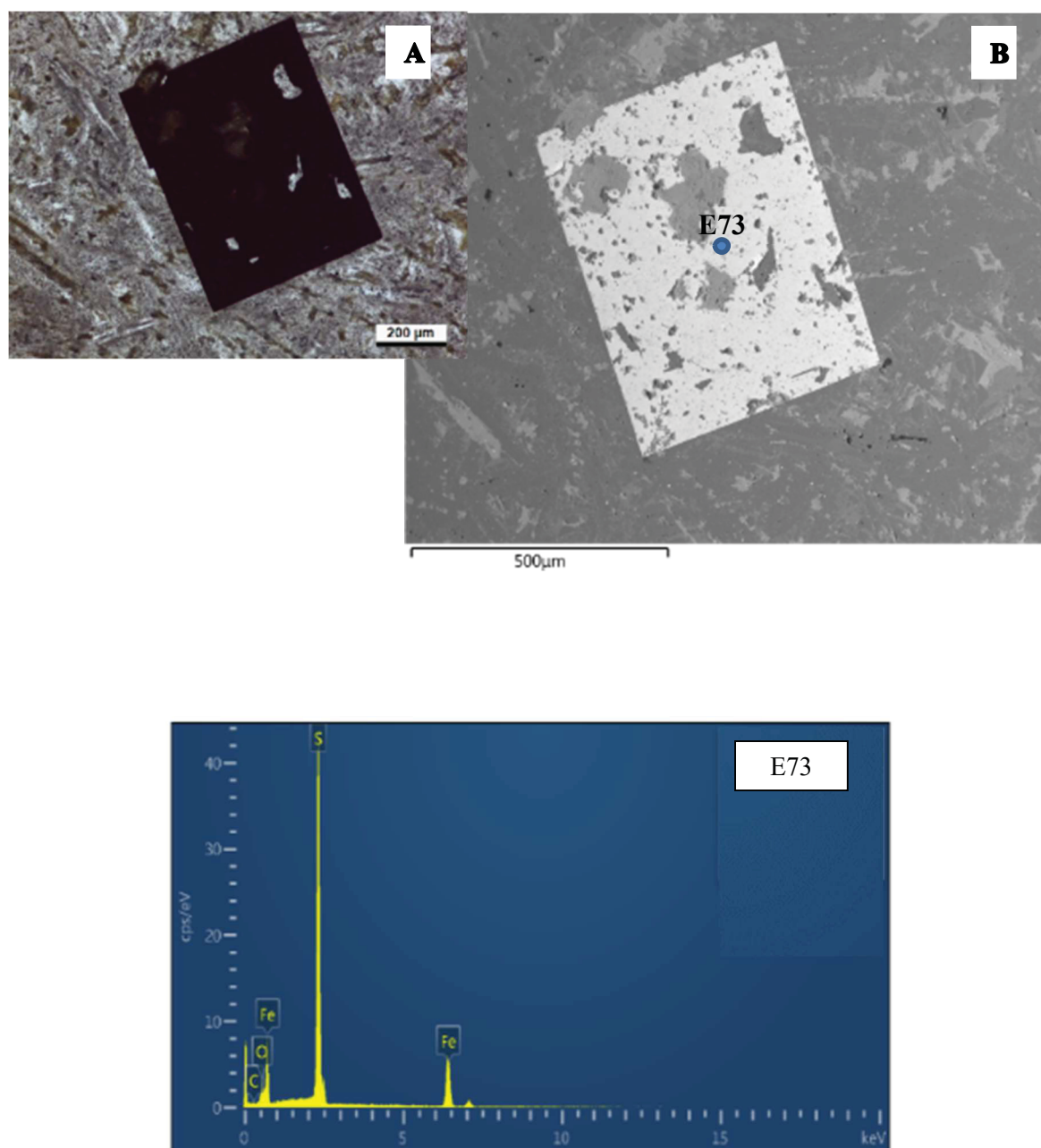


Figure 5.38. Hydrothermal rock in ICL4-F3. Photomicrographs (A) and BSE images (B) show the locations of the points of analysis. EDS spectrum of pyrite (E73).

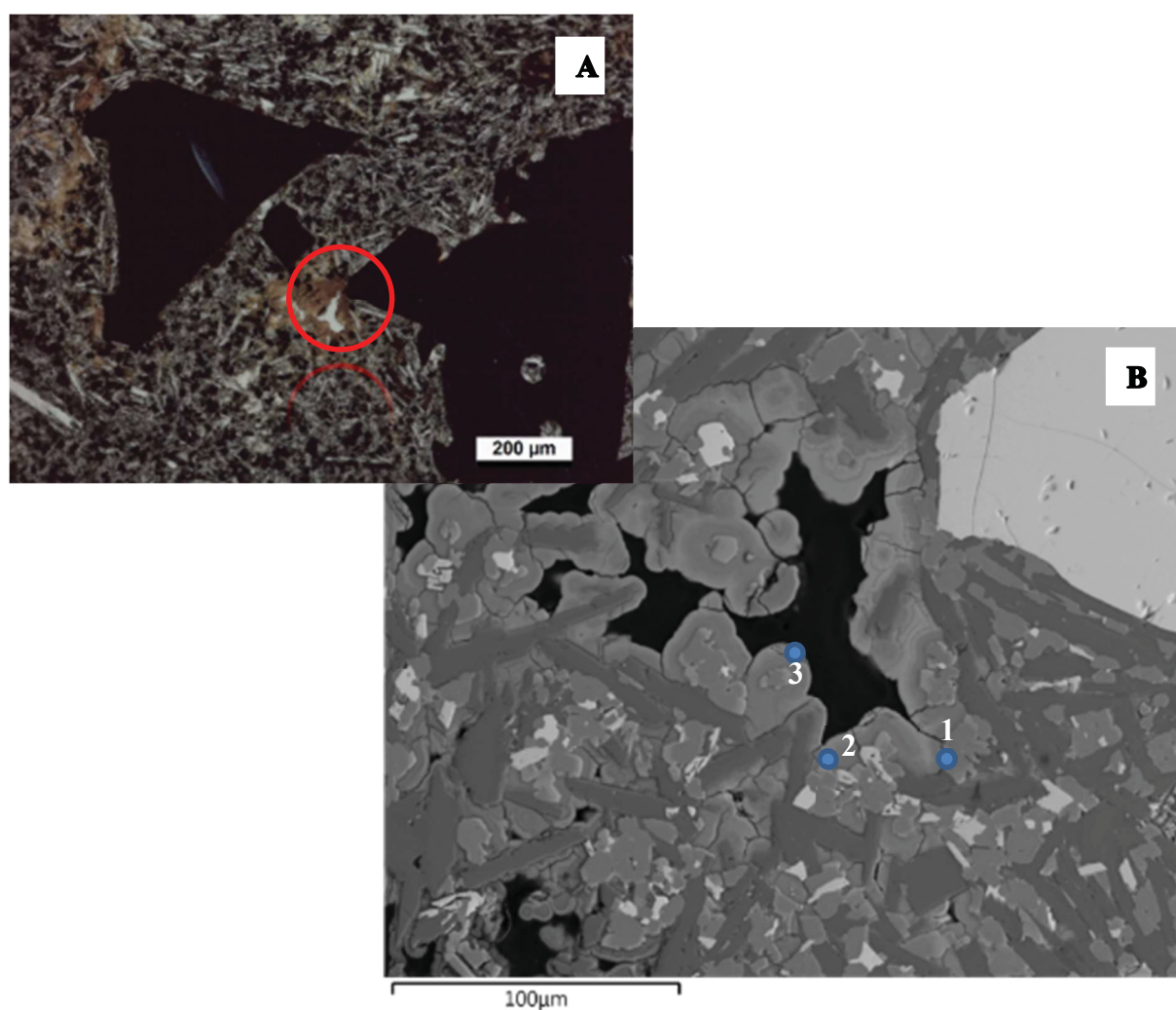


Figure 5.39. Basalt in ICL4-F3. Photomicrographs (A) and BSE images (B) with respective points of analysis.

Table 5.18. Sample ICL4-F3. EPMA-WDS results of volcanic glass (1- 3).

Oxides (%)	1	2	3
SiO ₂	46.63	46.04	45.02
TiO ₂	b.d.l.	2.68	b.d.l.
Al ₂ O ₃	2.73	2.05	1.36
FeO	34.04	34.77	38.20
MnO	0.07	0.07	b.d.l.
MgO	4.16	4.53	3.38
CaO	2.16	1.70	1.62
Na ₂ O	0.04	0.25	0.50
K ₂ O	0.18	0.44	0.64
Total	90.85	92.72	90.84

b.d.l = below detection limit

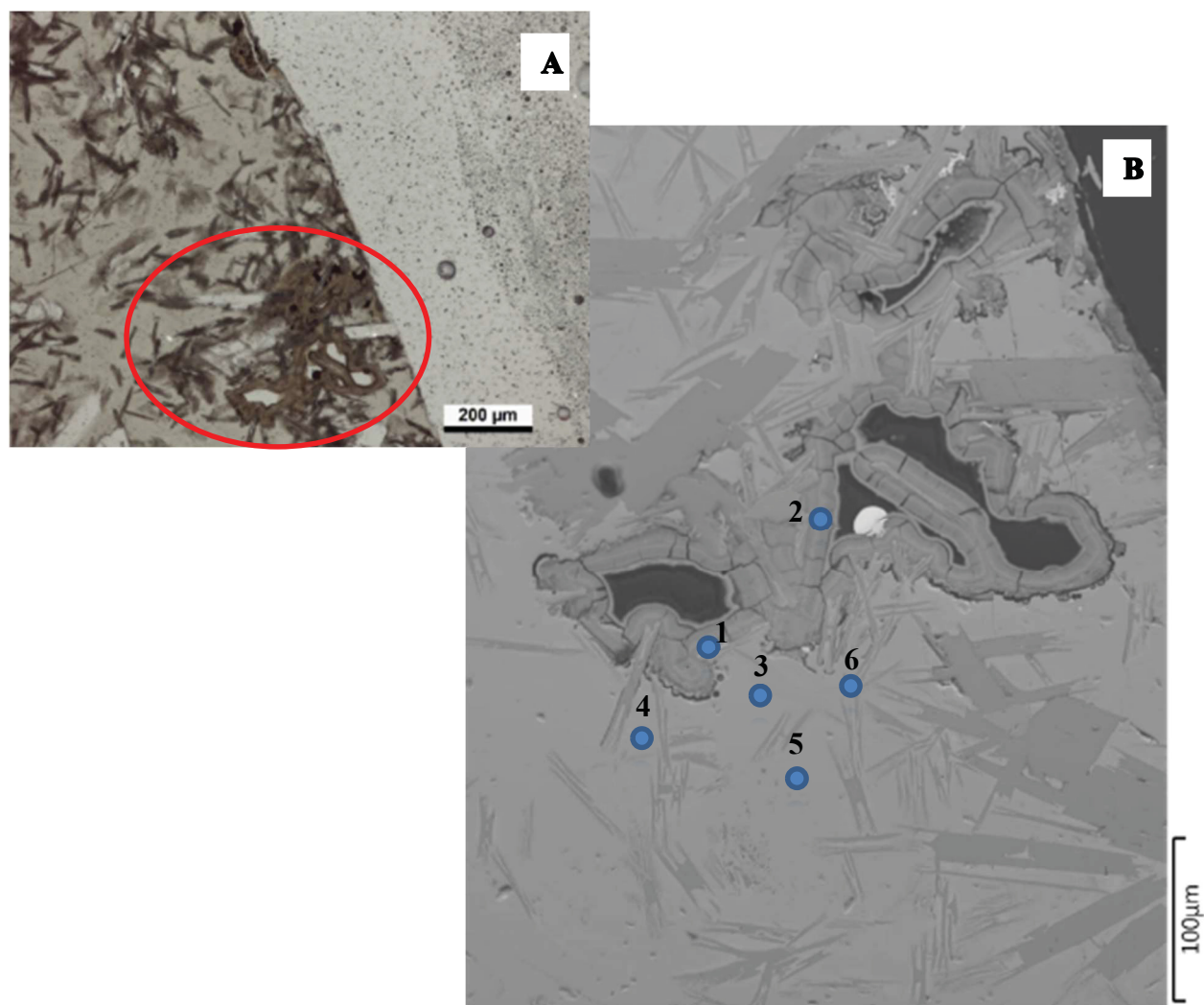


Figure 5.40. Glassy basalt in ICL4-F4. Photomicrographs (A) and BSE images (B) with respective points of analysis (1-6).

Table 5.19. Sample ICL4-F4. EMPA-WDS results of possibly smectite (1-2) and of volcanic glass (3-6).

Oxides (%)	1	2	3	4	5	6
SiO ₂	47.16	48.79	48.37	48.77	48.65	47.91
TiO ₂	b.d.l.	b.d.l.	1.60	1.54	1.60	1.60
Al ₂ O ₃	13.00	15.52	14.25	14.25	14.12	13.78
FeO	13.83	13.37	11.62	11.52	11.54	12.04
MnO	0.15	b.d.l.	0.18	0.23	0.14	0.19
MgO	12.83	9.23	7.63	7.53	7.42	7.81
CaO	1.86	1.78	11.65	11.75	11.76	11.63
Na ₂ O	0.13	0.50	2.11	2.21	2.16	2.17
K ₂ O	1.17	1.56	0.19	0.18	0.20	0.21
Total	90.23	91.00	97.78	98.08	97.72	97.56

b.d.l. = below detection limit

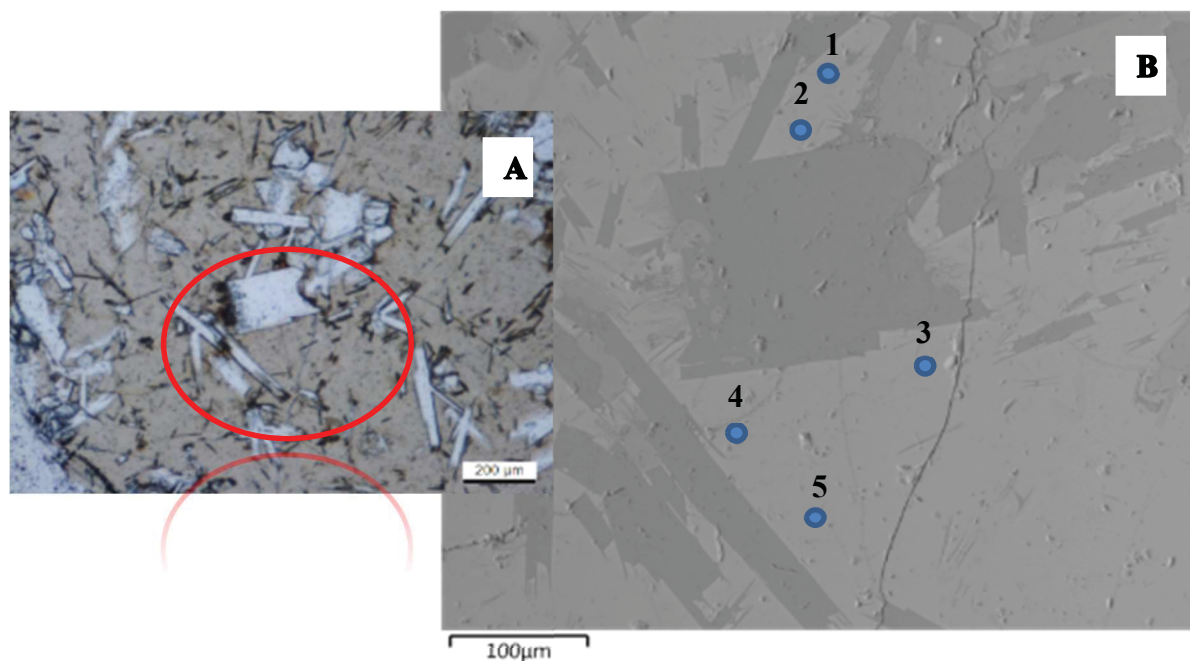


Figure 5.41. Glassy basalt in ICL4-F4. Photomicrographs (A) and BSE images (B) showing the points of analysis (1-5).

Table 5.20. Sample ICL4-F4. EPMA-WDS results of volcanic glass (1-5).

Oxides (%)	1	2	3	4	5
SiO ₂	48.77	48.33	48.58	48.49	48.74
TiO ₂	1.55	1.62	1.51	1.56	1.68
Al ₂ O ₃	13.67	14.05	14.15	14.15	14.09
FeO	11.81	11.58	11.50	11.58	11.54
MnO	0.18	0.17	0.17	0.18	0.17
MgO	8.06	7.56	7.56	7.69	7.53
CaO	11.38	11.57	11.68	11.69	11.48
Na ₂ O	2.06	2.07	2.17	2.05	2.07
K ₂ O	0.23	0.21	0.19	0.20	0.20
Total	97.82	97.42	97.62	97.76	97.72

Japan

From the macroscopic point of view, the andesite is aphanitic with a light grey colour, although some particles have a reddish tone on some surfaces. In general, the aggregate particles are punctuated mainly by plagioclase white crystals and several dark crystals are also present.

The crushed rock forms subangular aggregate particles with some elongated shapes. Figure 5.42 shows the macroscopic aspect and detail of some of the andesitic aggregate particles.



Figure 5.42. Macroscopic photos of JAP aggregates: A) general view and B) detailed perspective.

The andesite (JAP) is highly porphyritic (Figure 5.43A) with phenocrysts of plagioclase, orthopyroxene (hypersthene), clinopyroxene (augite), very few crystals of amphibole (hornblende) (Figure 5.43B) and opaque minerals. The groundmass is composed of plagioclase, tridymite, pyroxene, opaque minerals and apatite.

Plagioclase phenocrysts are zoned and embayed and some show a thin sieve texture on the rim (Figure 5.43C). Plagioclase phenocrysts frequently form glomeroporphyric clots together with clinopyroxene and opaque minerals. Hypersthene is the most common pyroxene in JAP samples with greenish to pale reddish pleochroism and well-visible cleavage.

The groundmass contains several sections of a mineral with very low grey colours and moderate relief that by habit is compatible with tridymite (Figure 5.43D).

EDS was performed to confirm the composition of some very small crystals, namely the presence of tridymite (Figure 5.44A and B).

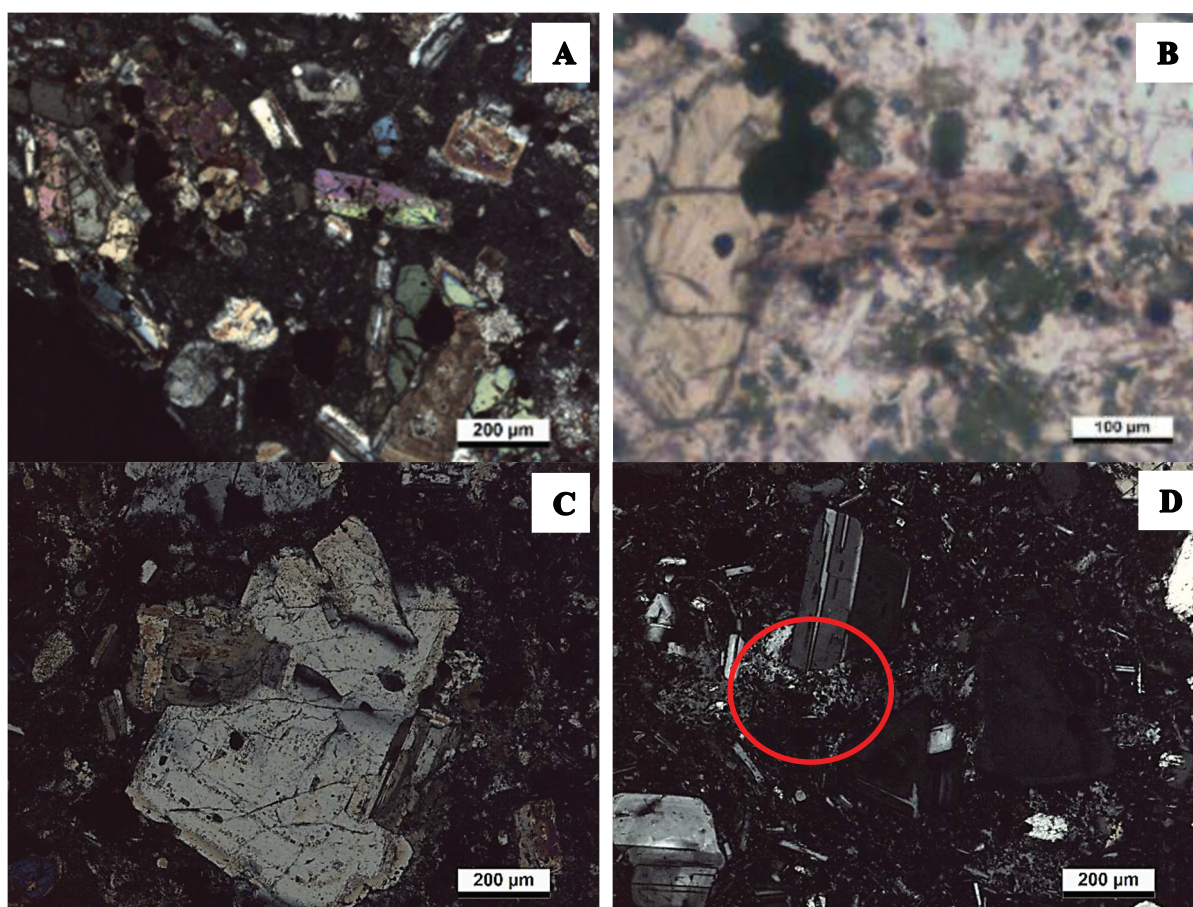


Figure 5.43. Photomicrographs of JAP andesite: A, C and D in XPL, B in PPL. A) Porphyritic texture; B) Amphibole (hornblende); C) Zoned plagioclase crystal with sieve texture; D) Section of the groundmass with tridymite.

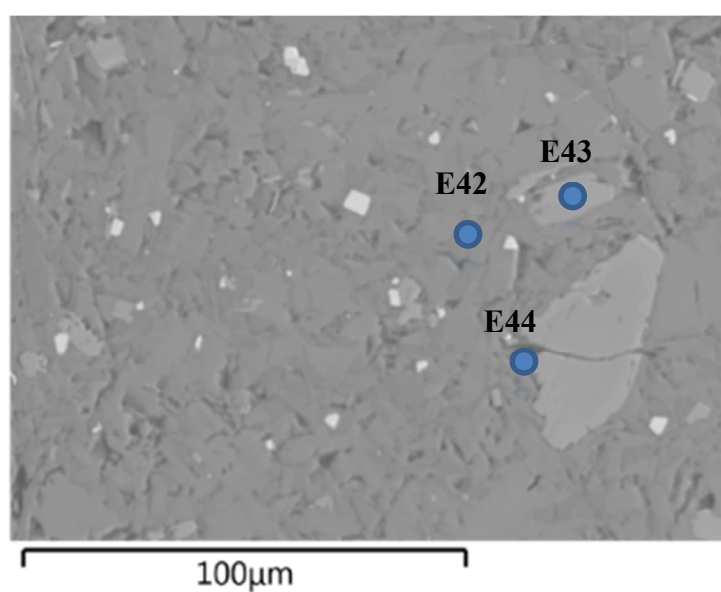


Figure 5.44A. Sample JAP (andesite). BSE image and respective points of analysis.

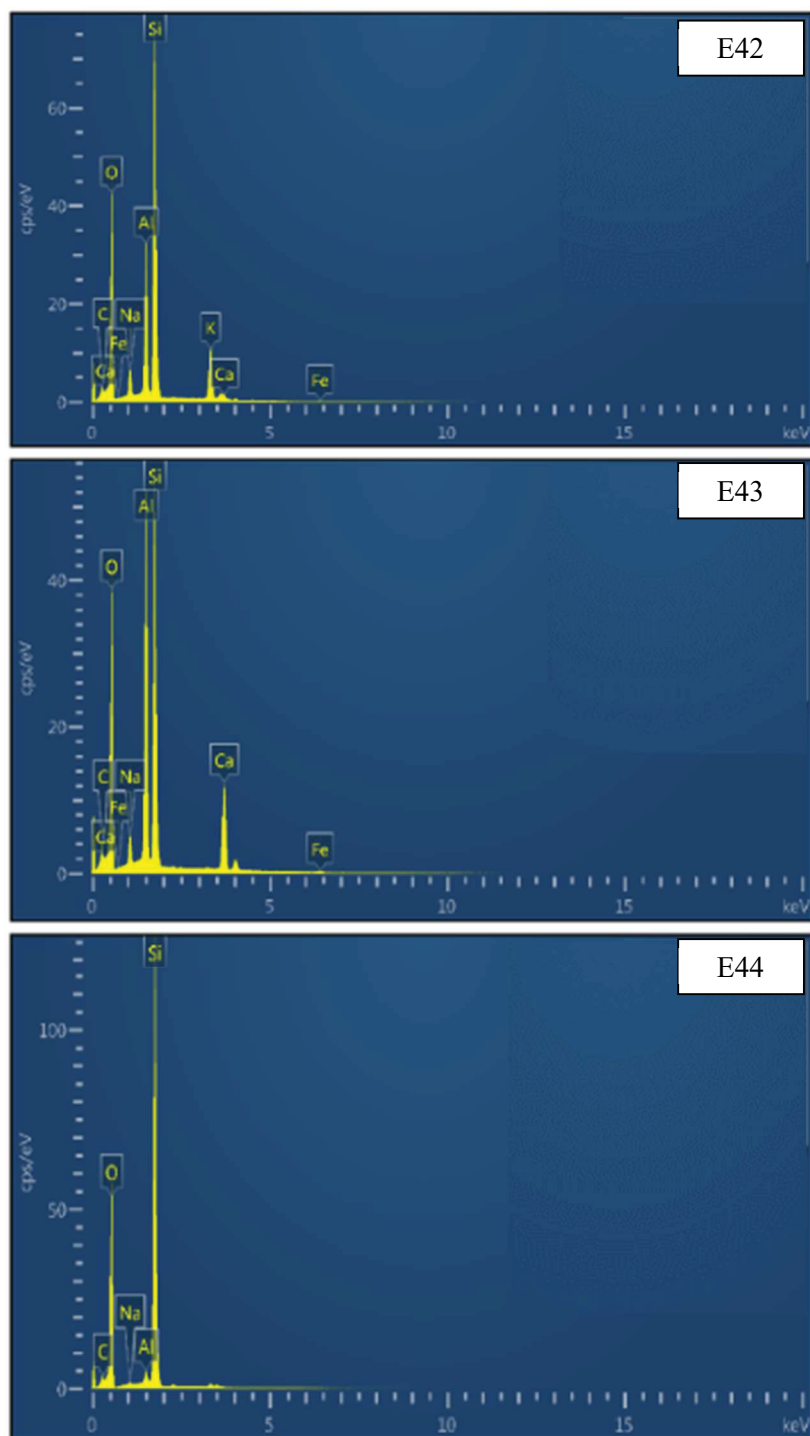


Figure 5.44B. Sample JAP (Andesite). EDS spectra of alkaline feldspar (E42), plagioclase (E43) and a silica mineral which might be tridymite (E44).

New Zealand

Macroscopically, the aggregate samples from New Zealand are aphanitic with phenocrysts of olivine and some plagioclase. The samples are light grey in colour, but some display a bluer-greyish colour (NZ2). All samples contain aggregate particles with a reddish tone and particles

that are more massive than others. NZ3 sample showed that the majority of the particles are elongated presenting a more subangular form. The three samples were grouped into different fractions based on the texture and colour: quite massive, vesicular and reddish particles (Figure 5.45).



Figure 5.45. Macroscopic photos of the different aggregates and facies from New Zealand.

Several aggregate particles were studied from the three rock samples (NZ1, NZ2 and NZ3). The basanite is porphyritic with phenocrysts of olivine and clinopyroxene, titanomagnetite and less frequent plagioclase. The matrix is formed by the same mineral assemblage and brownish volcanic glass (Figure 5.46A). In some aggregate particles, olivine appears significantly altered to iddingsite; others have embayments and skeletal textures. Besides iddingsite, other alteration products are present such as saponite which is filling some of the cracks in olivine (Figure 5.46B) and chlorite. The clinopyroxene shows a marked typical cleavage. In addition, some sections of the aggregate particles have vesicles filled with zeolites or/and carbonates (Figure 5.46C). In other particles, the groundmass is formed by a dark glass corresponding to tachylite. Chlorite and clay minerals are also visible in the interstices (Figure 5.46D) and vesicles of the rock (Figure 5.46E). In the matrix, a yellowish brown material is sometimes

observed, isotropic to slightly or complete anisotropic, that shows some degrees of crystallization, as described by Stroncik and Schmincke, (2007) (Figure 5.46F).

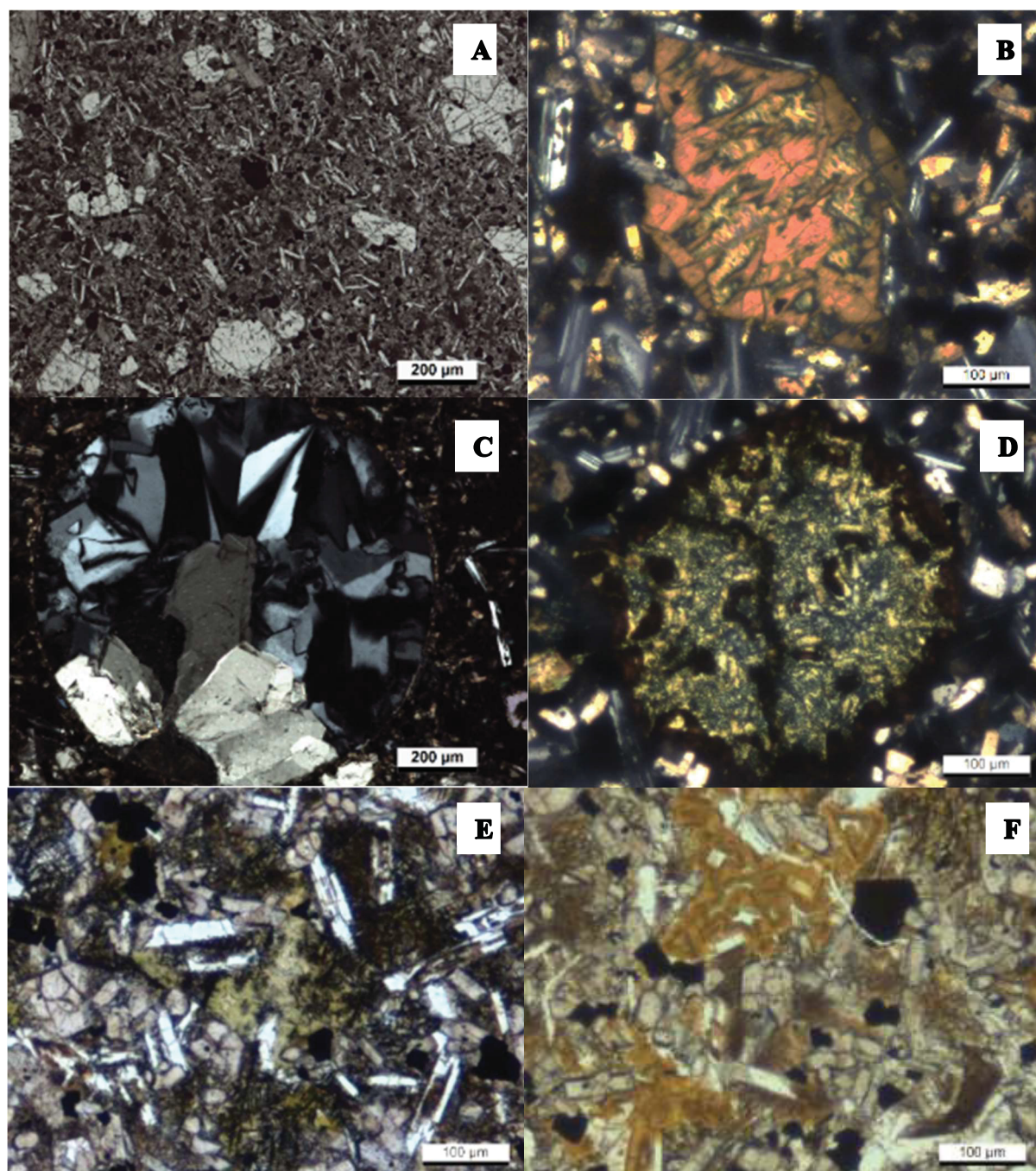


Figure 5.46. Photomicrographs of NZ1 sample: B, C and D in XPL, A, E and F in PPL. A) Porphyritic texture with brownish interstitial volcanic glass; B) Iddingsitized olivine with fractures filled with saponite; C) Vesicle filled with zeolite and carbonate; D) Vesicle filled with chlorite and clay minerals; E) Chlorite and smectite in the interstices of the rock; F) Volcanic glass (palagonite).

Further investigation was done by EPMA to identify different minerals and the volcanic glass, as well as zeolite and calcite filling a vesicle (Figure 5.47A and Table 5.21). Also EDS analysis was performed (Figure 5.47B) to identify zeolite and calcite.

Brownish volcanic glass and greenish chlorite-smectite minerals were also characterised by EPMA, as presented in Figure 5.48 and Table 5.22.

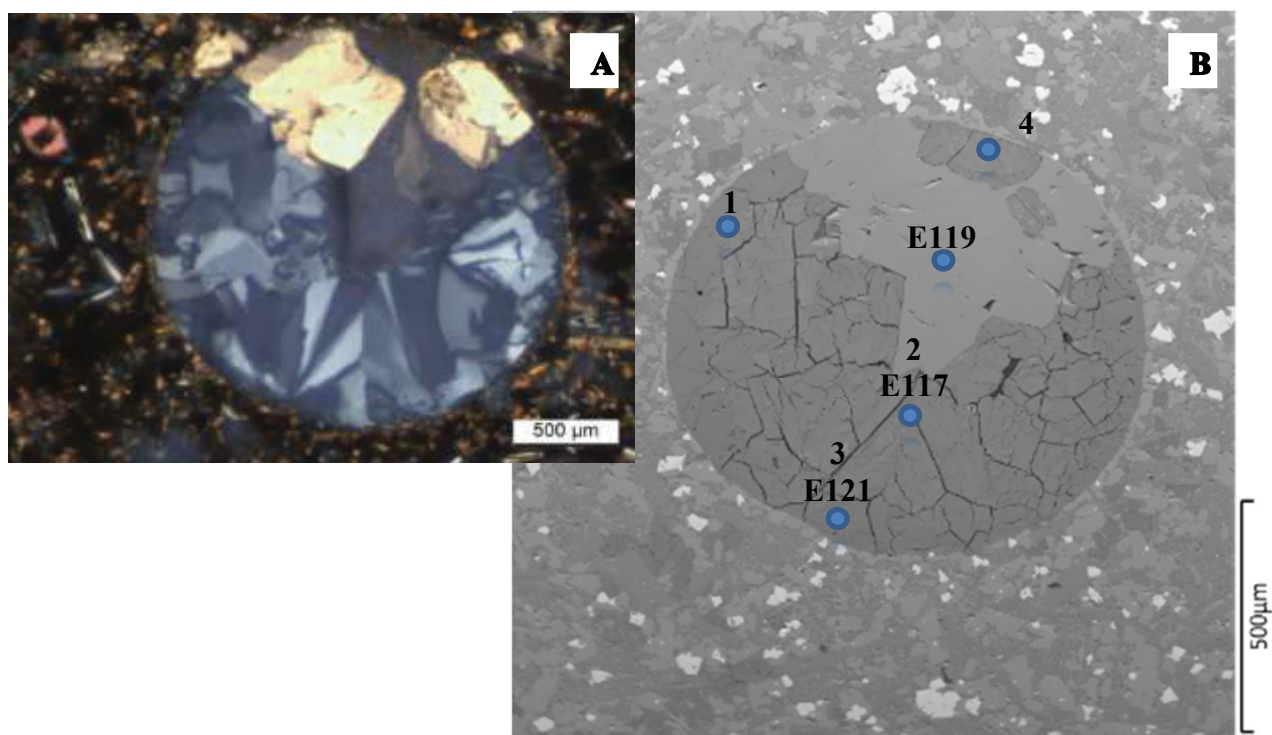


Figure 5.47A. Basanite NZ1. Microphotograph (A) and BSE image (B) and respective points of analysis.

Table 5.21. Sample NZ1. EPMA-WDS analyses of zeolite (1-4) filling a vesicle.

Oxides (%)	1	2 (E117)	3 (E121)	4
SiO ₂	52.54	50.73	52.05	49.09
TiO ₂	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al ₂ O ₃	22.83	24.38	27.08	22.88
FeO	b.d.l.	b.d.l.	b.d.l.	4.02
MnO	b.d.l.	b.d.l.	b.d.l.	0.91
MgO	b.d.l.	b.d.l.	b.d.l.	3.00
CaO	2.72	2.06	2.49	3.24
Na ₂ O	11.45	11.90	3.66	1.79
K ₂ O	2.84	6.07	6.09	5.50
Total	92.15	95.23	91.48	90.62

b.d.l = below detection limit

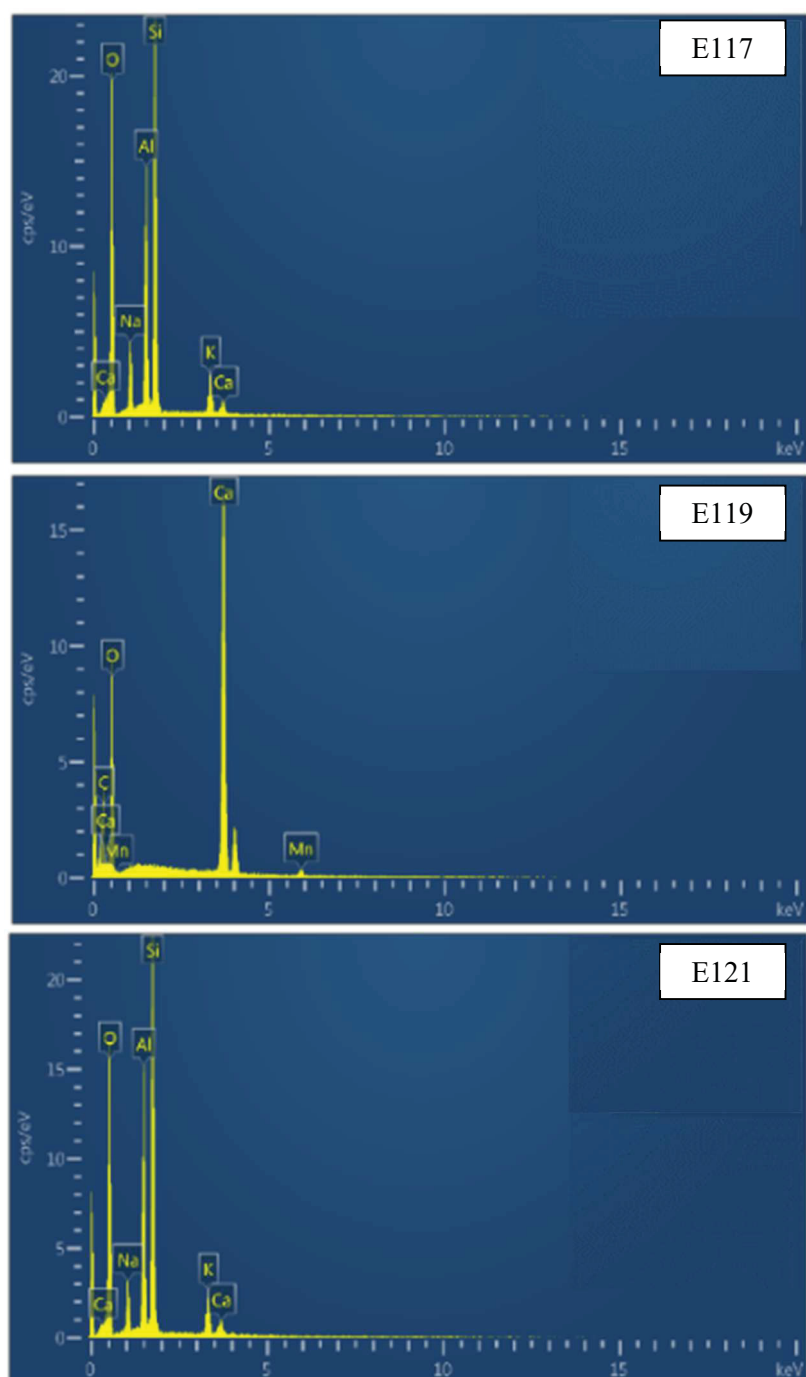


Figure 5.47B. EDS spectra of zeolite (E117 and E121) and calcite (E119).

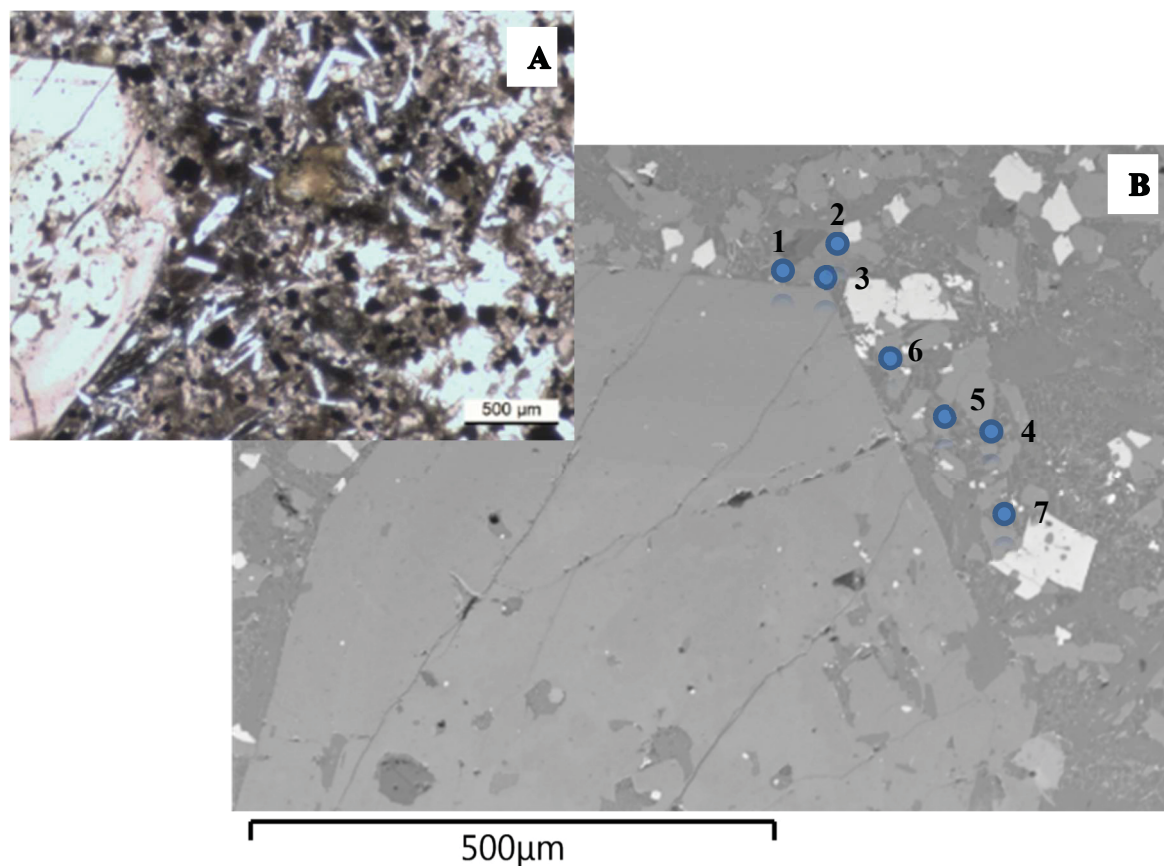


Figure 5.48. Basanite in NZ1. Photomicrograph (A), BSE image (B) and respective points of analysis.

Table 5.22. Sample NZ1. EMPA-WDS results of chlorite–smectite minerals (C/S) (1-3) and volcanic glass (4-8).

Oxides (%)	1	2	3	4	5	7	8
SiO ₂	34.97	35.83	39.31	52.50	52.56	51.76	50.79
TiO ₂	b.d.l.	0.14	0.14	0.11	0.23	0.85	0.60
Al ₂ O ₃	12.95	13.21	11.72	28.76	28.88	27.16	27.63
FeO	22.09	22.84	21.78	2.20	1.37	3.79	1.53
MnO	0.30	0.29	0.29	b.d.l.	b.d.l.	0.16	b.d.l.
MgO	18.15	15.30	16.76	1.68	1.00	0.84	0.74
CaO	0.58	0.73	0.81	0.40	0.36	0.34	1.34
Na ₂ O	b.d.l.	b.d.l.	0.16	7.13	8.46	9.46	10.55
K ₂ O	0.12	0.12	0.27	2.13	2.91	2.66	2.89
Total	89.32	88.62	91.30	95.04	96.00	97.20	96.20

b.d.l = below detection limit

The NZ2 sample is highly porphyritic (Figure 5.49A) with phenocrysts of plagioclase and olivine and less amount of clinopyroxene. The matrix is formed by plagioclase, clinopyroxene, olivine and opaque minerals.

Plagioclase forms the most common phenocryst phase with composition ranging from labradorite to bytownite, with euhedral to subhedral crystals and some zonation patterns. In several sections, there are glomeroporphyritic clusters either in monomineralic aggregates (Figure 5.49B) or together with olivine and clinopyroxene (Figure 5.49C). Olivine crystals are typically euhedral with some embayments. Clinopyroxene is normally augite (Figure 5.49D), mainly euhedral-subhedral and usually twinned.

The volcanic glass was not identified in this aggregate.

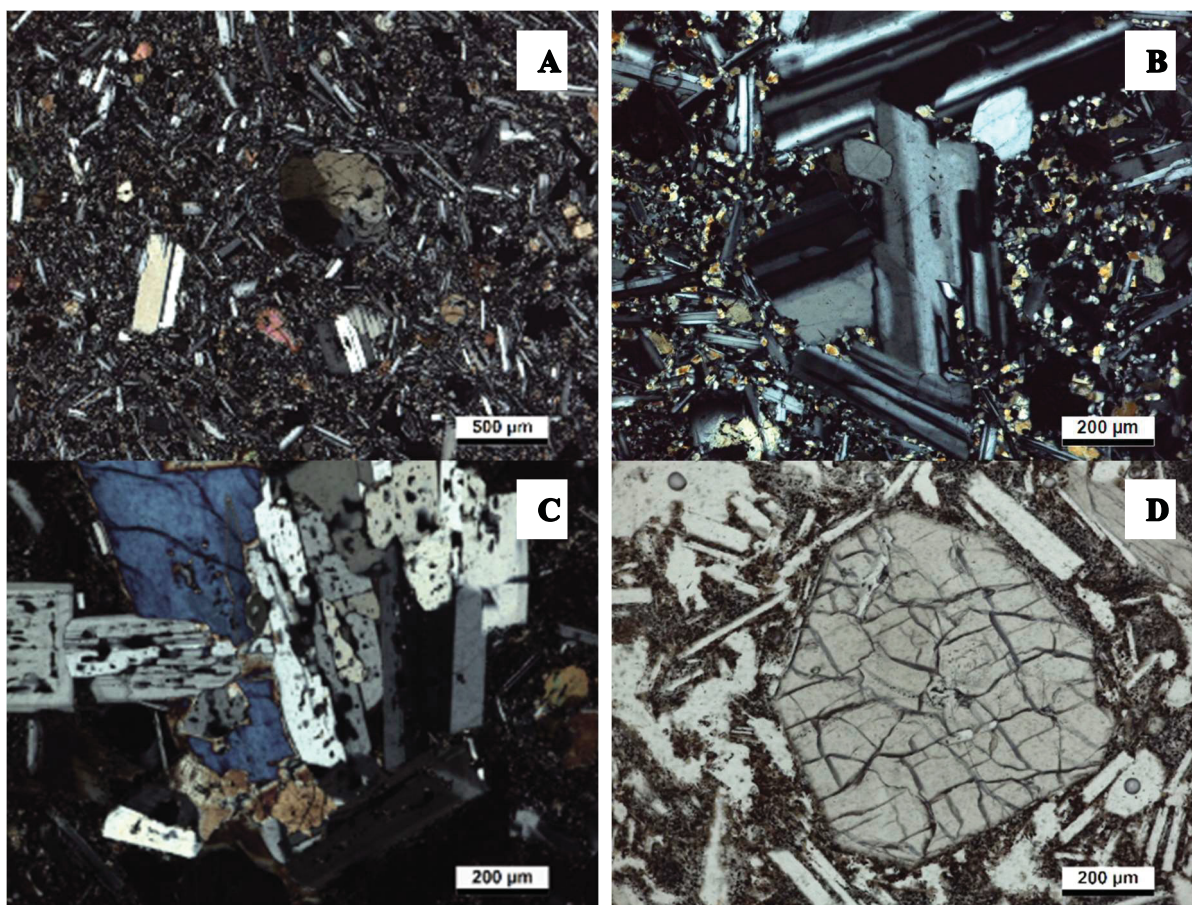


Figure 5.49. Photomicrographs of NZ2 sample. All photos are in XPL. A) Porphyritic texture; B) Glomeroporphyritic clots of plagioclase; C) Glomeroporphyritic clots of plagioclase and olivine; D) Clinopyroxene.

The NZ3 sample is also porphyritic but some of the particles seem to have a coarser groundmass (plagioclases with $d \pm 50 \mu\text{m}$) when compared to other aggregate particles (Figure 5.50A and B). Also, subophitic textures are present. The phenocrysts are composed mainly of olivine set in a fine-grained matrix of plagioclase and clinopyroxene (augite). Olivine represents the main phenocryst phase in euhedral to subhedral crystals with embayments and sometimes skeletal textures. Some olivine appears in agglomerates forming glomeroporphyritic clusters, sometimes together with plagioclase. The plagioclase crystals are more calcic in composition, with laths of labradorite either in the matrix or in pheno/microphenocrysts. Some crystals are zoned. The opaque minerals are scattered in the rock showing sometimes skeletal texture. The presence of volcanic glass was identified in some of the aggregate particles. Part of this glass is tachylite with a dark colour in PPL and it is present in some of the aggregate particles with vesicles (Figure 5.50C). In other aggregate particles, yellow to brownish glass is sometimes present in the interstices of the plagioclase crystals (Figure 5.50D).

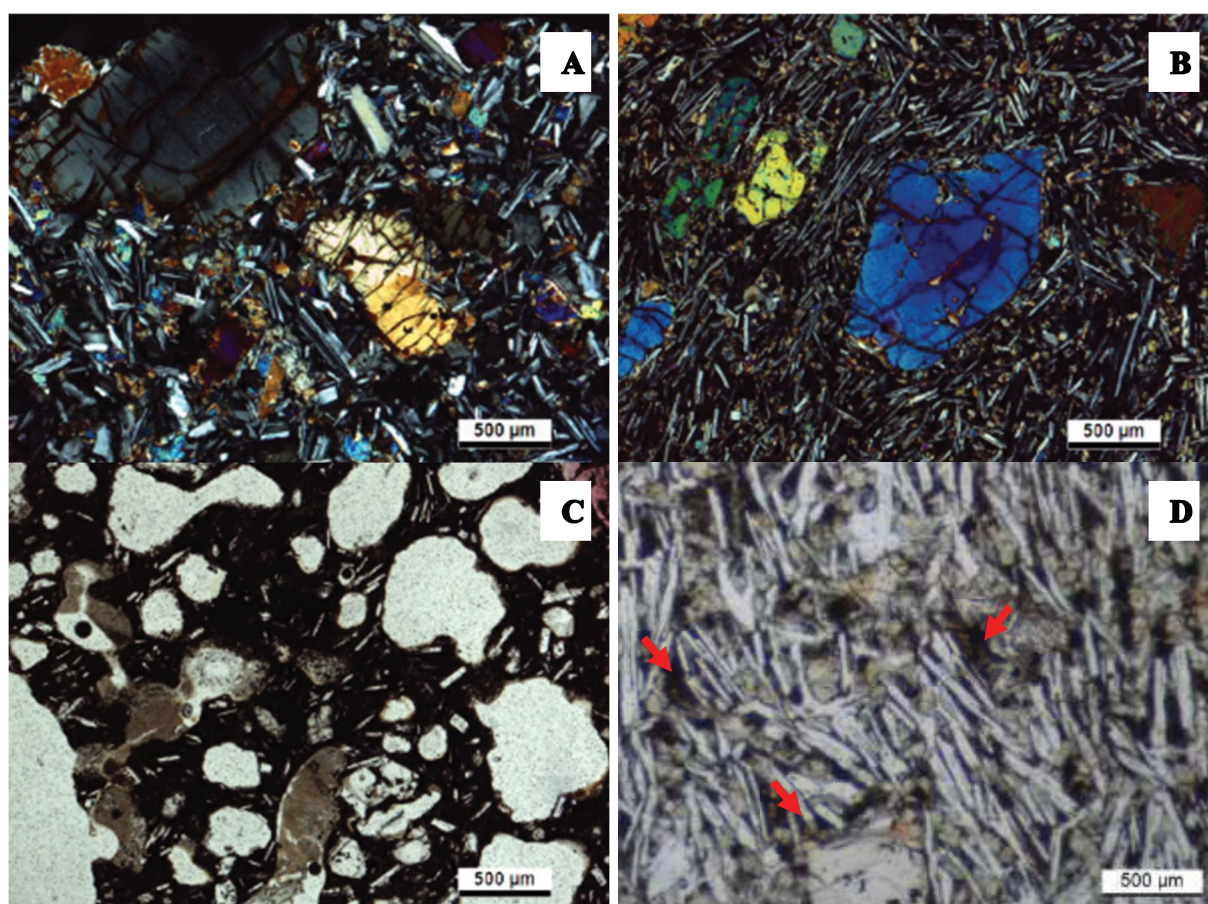


Figure 5.50. Photomicrographs of NZ3 sample: A and B in XPL; C and D in PPL. A) Porphyritic texture and subophitic textures in a coarser matrix; B) Porphyritic texture in a fine-grained matrix; C) Tachylite in a vesicular aggregate particular; D) Interstitial volcanic glass indicated by red arrows.

Further analyses were performed in volcanic glass by EPMA (Figures 5.51, 5.52 and 5.53, and Tables 5.23, 5.24 and 5.25).

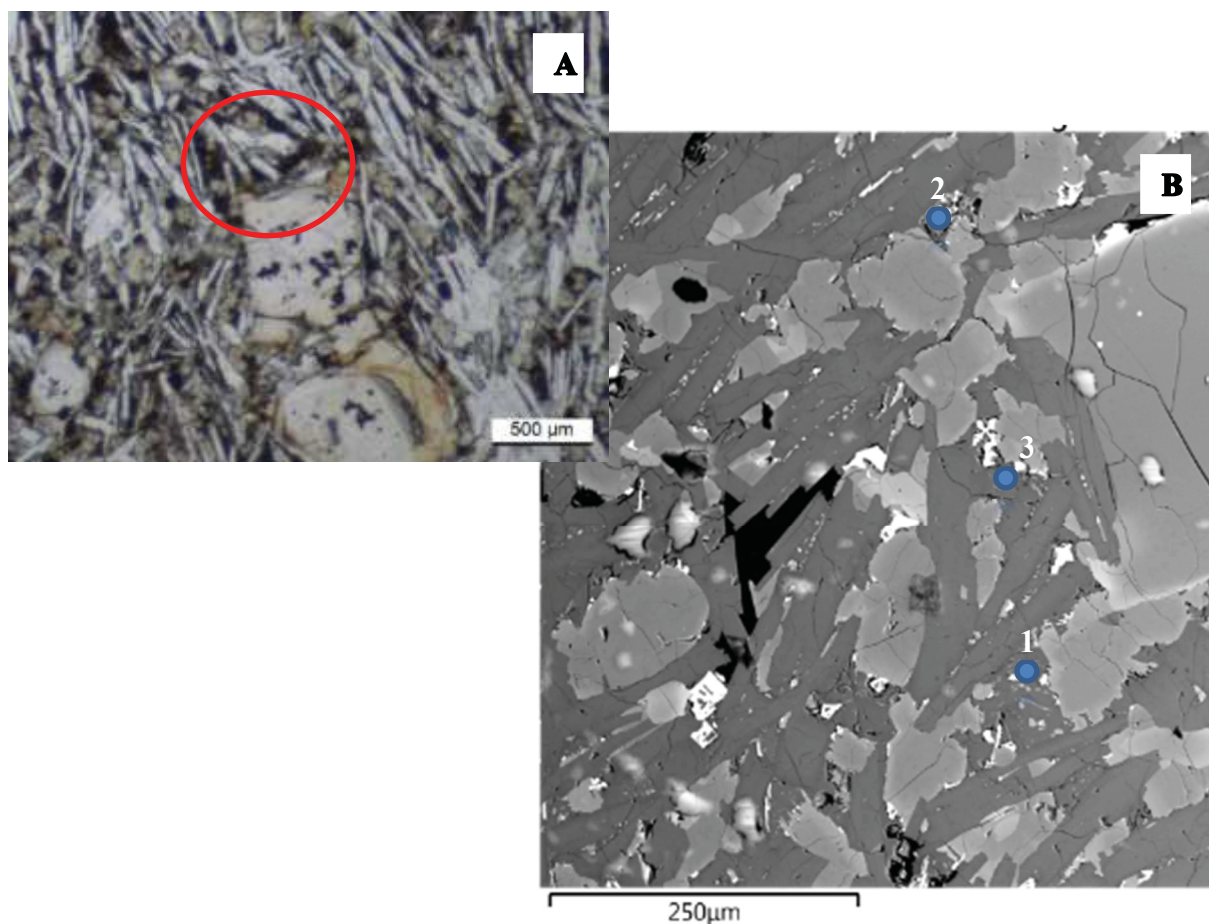


Figure 5.51. Basalt of NZ3. Photomicrograph (A) and BSE image (B) and respective points of analysis (1-3).

Table 5.23. Sample NZ3. EMPA-WDS analyses of volcanic glass (1-3) in figure 5.51.

Oxides (%)	1	2	3
SiO ₂	70.89	66.54	67.54
TiO ₂	1.23	0.93	0.96
Al ₂ O ₃	14.50	13.70	13.53
FeO	2.68	1.67	2.30
MnO	0.10	b.d.l.	b.d.l.
MgO	b.d.l.	b.d.l.	b.d.l.
CaO	1.17	1.84	3.71
Na ₂ O	1.42	1.61	2.41
K ₂ O	2.67	5.49	3.40
Total	95.99	92.40	94.96

b.d.l = below detection limit

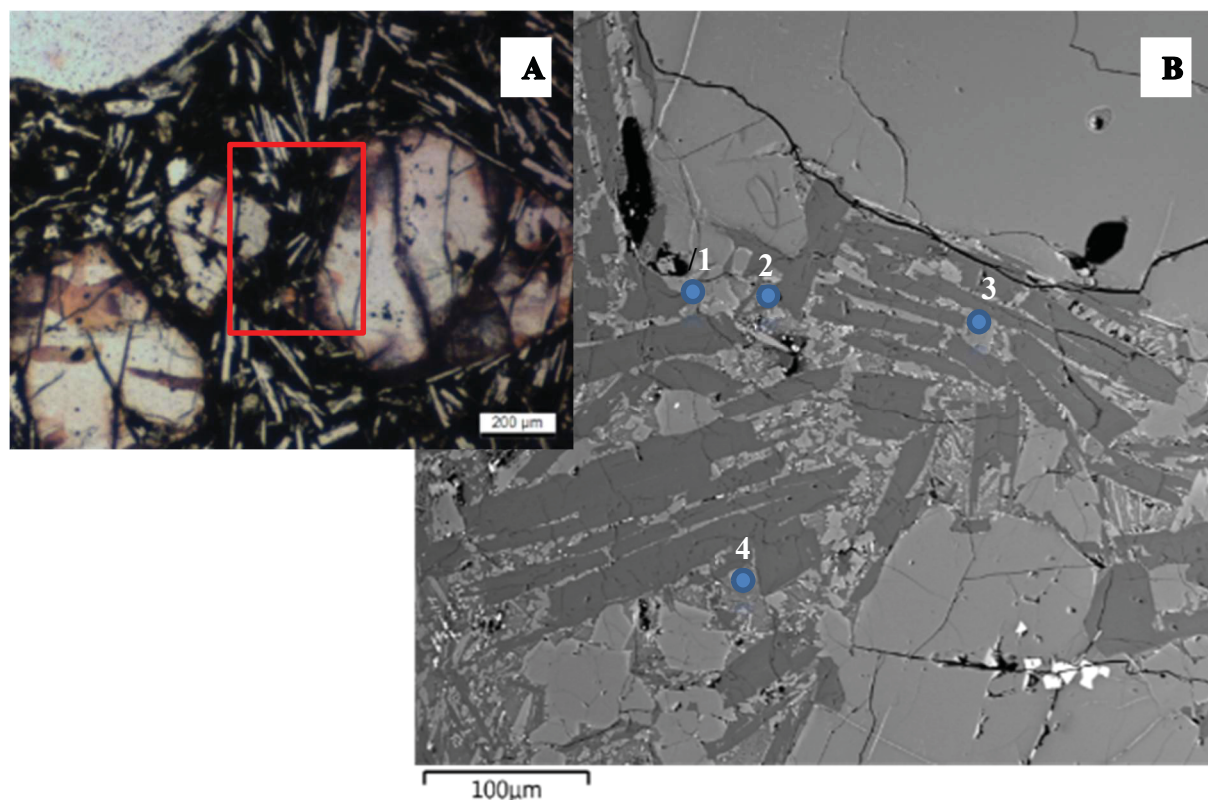


Figure 5.52. Basalt in NZ3. Photomicrograph (A) and BSE image (B) and points of analysis of volcanic glass (1-4).

Table 5.24. Sample NZ3. EPMA-WDS analyses of volcanic glass (1-4) of Figure 5.52.

Oxides (%)	1	2	3	4
SiO ₂	57.63	55.42	60.09	59.68
TiO ₂	3.26	3.63	2.62	2.05
Al ₂ O ₃	12.29	11.10	11.49	16.64
FeO	10.47	14.25	11.67	8.36
MnO	0.19	0.27	0.18	b.d.l.
MgO	1.21	1.48	1.56	0.71
CaO	5.65	4.83	5.10	5.04
Na ₂ O	2.36	2.37	2.82	4.02
K ₂ O	1.87	3.30	0.67	0.69
Total	95.27	96.99	96.64	97.68

b.d.l. = below detection limit

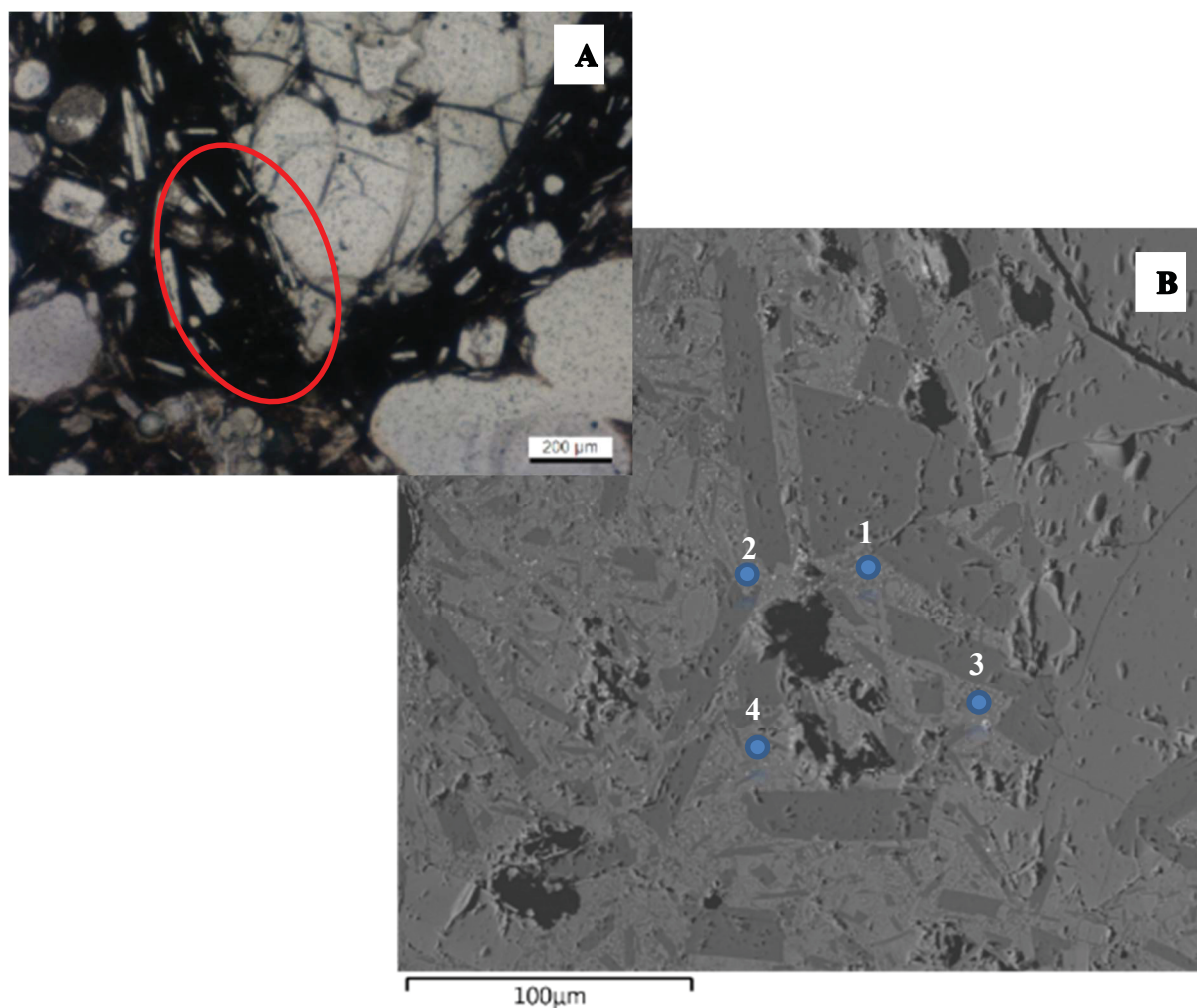


Figure 5.53. Basalt in NZ3. Photomicrograph (A) and BSE image (B) and respective points of analysis (1-4).

Table 5.25. Sample NZ3. EMPA-WDS analyses of volcanic glass (1-4) of figure 5.53.

Oxides (%)	1	2	3	4
SiO ₂	54.33	53.04	55.52	53.37
TiO ₂	2.07	2.36	1.90	1.85
Al ₂ O ₃	12.43	12.81	11.42	14.29
FeO	14.07	12.67	11.89	13.23
MnO	0.26	0.25	0.24	0.21
MgO	3.01	2.39	5.53	5.03
CaO	6.95	6.43	8.15	10.13
Na ₂ O	2.22	1.62	1.63	1.60
K ₂ O	1.26	1.48	1.43	0.83
Total	96.90	93.39	97.95	100.0

5.1.3. Mortar studies

5.1.3.1. Expansion tests - Accelerated mortar-bar test at 80°C (CSA A23.2-25A/ASTM C 1260)

Different accelerated mortar bar tests were performed as part of the present study. Thirty mixes were done at Université Laval, in Québec, Canada, and thirteen mixes in the National Laboratory for Civil Engineering (LNEC), in Lisbon, Portugal. The last ones (aggregates from the Azores) were conducted within the scope of the ReAVA (2012-2014) and IMPROVE (2010-2014) research projects, except the aggregate from Corvo Island (CRV) which was prepared in the scope of the current study. The Spratt and the GBS sand were used as references for each test. The characteristics of the mortar composition are presented in Table 4.13 in Chapter 4. The AMBT method is described by the CSA A23.2-25A (2019), ASTM C 1260 and RILEM AAR-2 (2016) but the limits are provided by the CSA Standard Practice A23.2-27A (2019), ASTM C 1778 (2020) and RILEM AAR-0 (2016).

Azores Archipelago (Portugal)

The results obtained after 14 days show (Figure 5.54) that most of the samples have expansion between 0.01% (SMA-SM2, GRA-SM1, SJO-SM1, FAI-SM1, FLO-SM1 and FLO-SM2) and 0.02% (SMA-SM1, SMG-SM1, SMG-SM2, SMG-SM3, TER-SM2 and CRV); PIC-SM1 did not show any expansion. At 28 days of testing, the values did not change significantly. After 128 to 140 days of testing, the expansion of the thirteen aggregates maintained the same pattern (0.01-0.08%), except for TER-SM1 (trachyte) which continued to increase with time with a long and progressive trend towards levelling off.

According to the different standards and recommendations, after 14 days of testing, the majority of these volcanic aggregates display expansion lower than the threshold of 0.10% (ASTM C 1778, 2020) and 0.15% (CSA 23.2-27A; RILEM AAR-0, 2016) which classifies the samples as non-reactive.

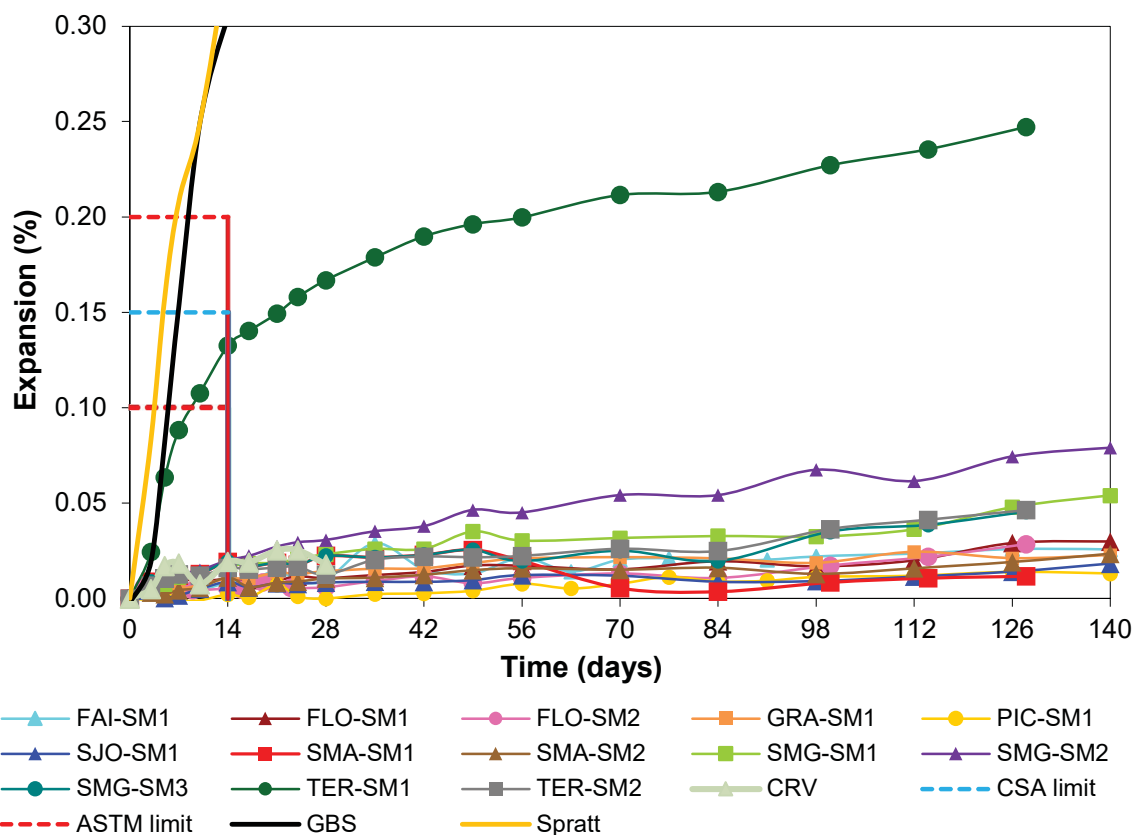


Figure 5.54. Expansion results of the accelerated mortar-bar test at 80°C concerning the Azorean aggregates: thirteen aggregates according to ASTM C 1260 and CRV aggregate according to CSA A23.2-25A.

The TER-SM1 aggregate displays an expansion of 0.13% at the end of 14 days. According to the Canadian standard, the TER-SM1 aggregate is considered non-reactive ($< 0.15\%$), while the RILEM recommendation AAR-2 (2016) would classify it as potentially reactive. For the American standard, this aggregate can be considered either innocuous or deleterious in field performance (uncertain zone). An extension of the testing period to 28 days is recommended and supplementary information should be obtained (e.g. petrographic examination of the aggregate, examination of the mortar bar after testing). At the end of 28 days, the expansion is still increasing (0.17%) and continued until the end of the test at 128 days (0.25%).

The expansions obtained with the reference Spratt and GBS aggregates were way beyond the threshold values at 14 days, with expansion values of 0.39% and 0.30%, respectively.

Canary Archipelago (Spain)

At 14 days, the aggregates CANY1 and CANY2 present low expansion, of 0.01% and 0.02%, respectively (Figure 5.55).

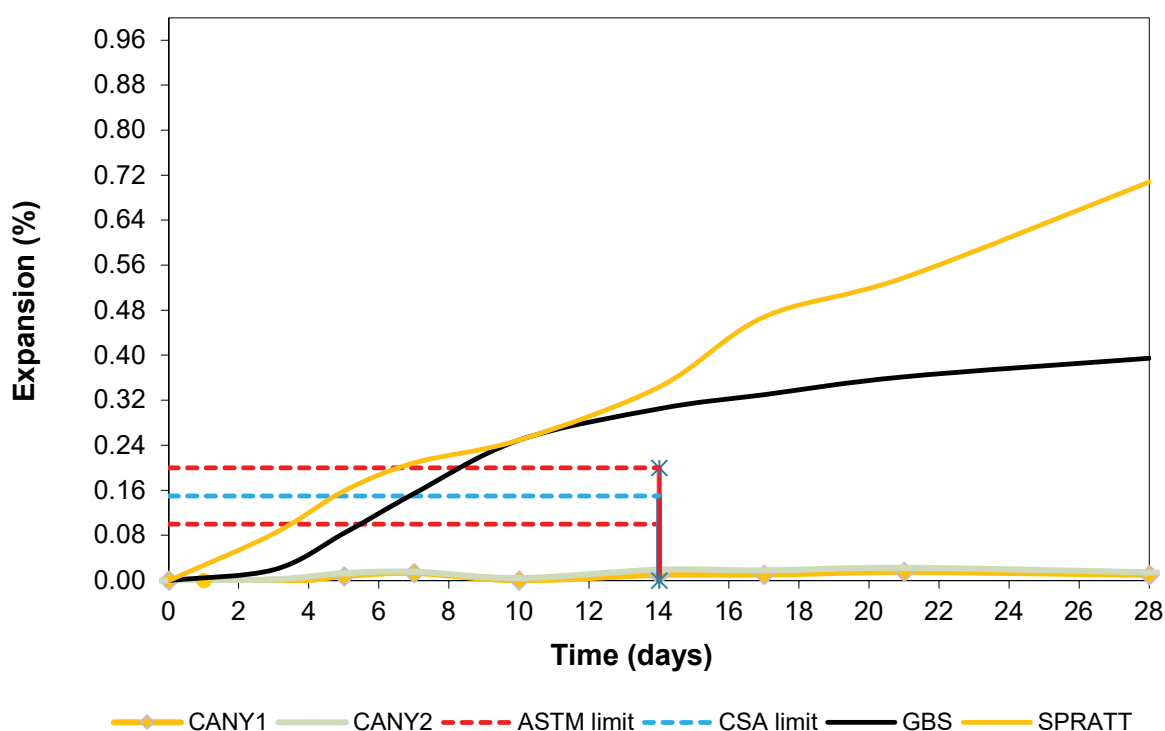


Figure 5.55. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Canary aggregates (CANY1 and CANY2).

The testing continued until 28 days and the expansion values were kept constant at 0.01%. Expansion is below the limiting value (0.10 %) for both samples, classifying the aggregates as non-reactive according to the American and Canadian standards and the RILEM recommendations.

Hawaiian Islands (USA)

The results obtained after 14 days show (Figure 5.56) that the majority of the aggregates present high expansion, with values higher than the limits indicated in the standards: HW1- 0.77%, HW3 - 0.82%, HW5 and HW6 - 0.45%, HW7- 0.66% and HW7 sand - 0.51%. The remaining aggregates display low expansion with values below the limit of 0.10%: HW2 -

0.07%, HW4 – 0.03% and HW4 sand – 0.02%. At the end of 28 days of testing, the expansion continued to increase for the aggregates that had high expansion at 14 days (HW1 – 1.13%, HW3 – 1.58%, HW5 and HW6 – 1.05%, HW7 – 1.25% and HW7 sand – 1.04%) with no signs of stabilization. For the others, the expansion kept constant values (0.02%-0.07%).

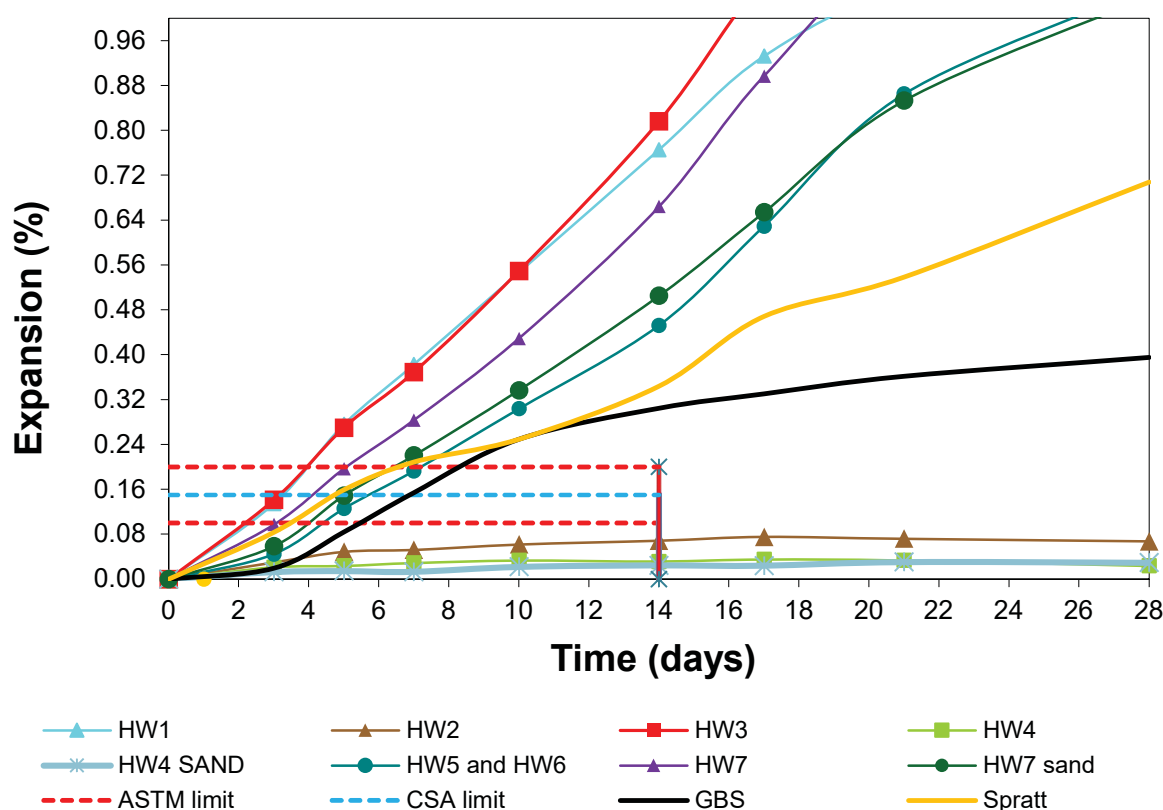


Figure 5.56. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Hawaiian aggregates.

According to the different standards and recommendations, after 14 days of testing, most of the volcanic aggregates are classified as potentially reactive, with expansion higher than 0.20% (ASTM C 1778, 2020; RILEM AAR-0, 2016), and even extremely reactive with expansion higher than 0.44% (CSA 23.2-27A, 2019), which is the case for the aggregates HW1, HW3, HW5 and HW6, HW7 and HW7 sand. The rest are considered non-reactive according to the same standards and recommendations, with expansion values lower than 0.10%.

Iceland

The results of the AMBT show that the majority of the Icelandic aggregates have high to moderate expansion and only one of the aggregates displays low expansion (Figure 5.57). At

14 days, the aggregates ICL1, ICL1 coarse and fine sand, ICL4 and ICL4 sand are the ones with the highest expansion: ICL1 – 0.44%; ICL1 coarse sand – 0.34%; ICL1 fine sand – 0.46%; ICL4 – 0.57% and ICL4 sand – 0.63%. The ICL3 and ICL3 sand aggregates show an expansion of 0.10% and 0.13%, respectively. ICL2 presents an expansion value of 0.05%. After 28 days of testing, the expansion of all aggregates continued to increase but with a tendency of stabilization: ICL1 – 0.58%; ICL1 coarse sand – 0.48%; ICL1 fine sand – 0.64%; ICL4 – 0.75%; ICL4 sand – 0.91%; ICL3 – 0.20%; ICL3 sand – 0.20% and ICL2 – 0.08%.

According to the American standard (ASTM C 1260, 2014) and the RILEM recommendations (RILEM AAR-2, 2016), the aggregates ICL1, ICL1 coarse and fine sand, ICL4 and ICL4 sand are considered potentially reactive, with expansion higher than 0.20%. For the Canadian standards (CSA A23.2-25A, 2019; CSA 23.2-27A, 2019), the aggregates ICL1, ICL1 fine sand, ICL4 and ICL4 sand are considered extremely reactive while ICL1 coarse sand is considered highly reactive.

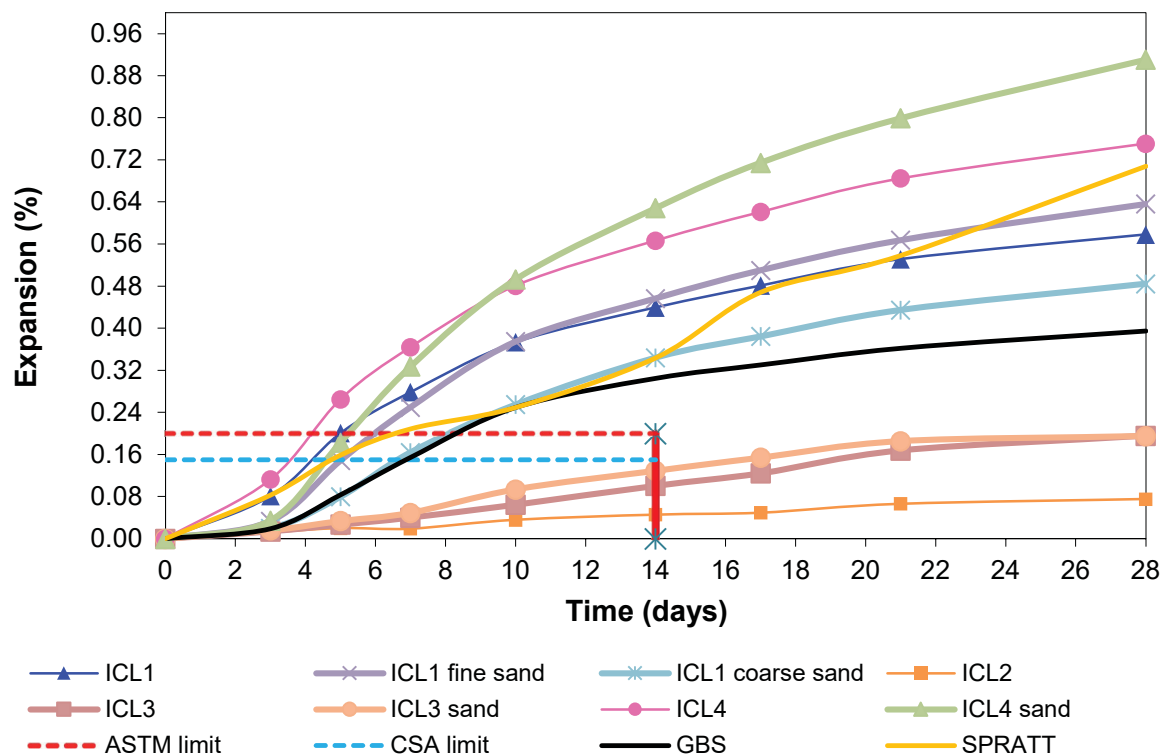


Figure 5.57. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the Icelandic aggregates.

For aggregates ICL3 and ICL3 sand, for which expansion ranges between 0.10 and 0.20%, the American standard considers these aggregates either innocuous or deleterious in field performance. An extension of the testing period to 28 days is recommended by the standard and supplementary information should be obtained (e.g. petrographic examination of the

aggregate, examination of the mortar bar after testing). In the absence of additional local experience, RILEM AAR-2 (2016) considers these two aggregates (ICL3 and ICL3 sand) potentially reactive. On the other hand, the Canadian standard classifies both aggregates (ICL3 and ICL3 sand) as non-reactive ($< 0.15\%$).

The aggregate ICL2 is considered non-reactive for both standards and also for the RILEM recommendation, with expansion lower than 0.10% even at 28 days.

The graphic shows that all aggregates seem to start gaining a stabilization tendency with time

Japan

The results of the AMBT for the Japanese aggregate indicate high expansion. At 14 days, the mortar bar with JAP shows an expansion value of 0.79% and continued to increase even at the end of 28 days of testing, reaching an expansion of 1.31% . The expansion is not showing a trend for stabilization with time. According to the standard ASTM C 1260 (2014) and recommendation RILEM AAR-2 (2016), this aggregate is considered potentially reactive, while it is considered extremely reactive according to the CSA A23.2-25A (2019). The results of the accelerated mortar-bar method for the Japan aggregate are shown in Figure 5.58.

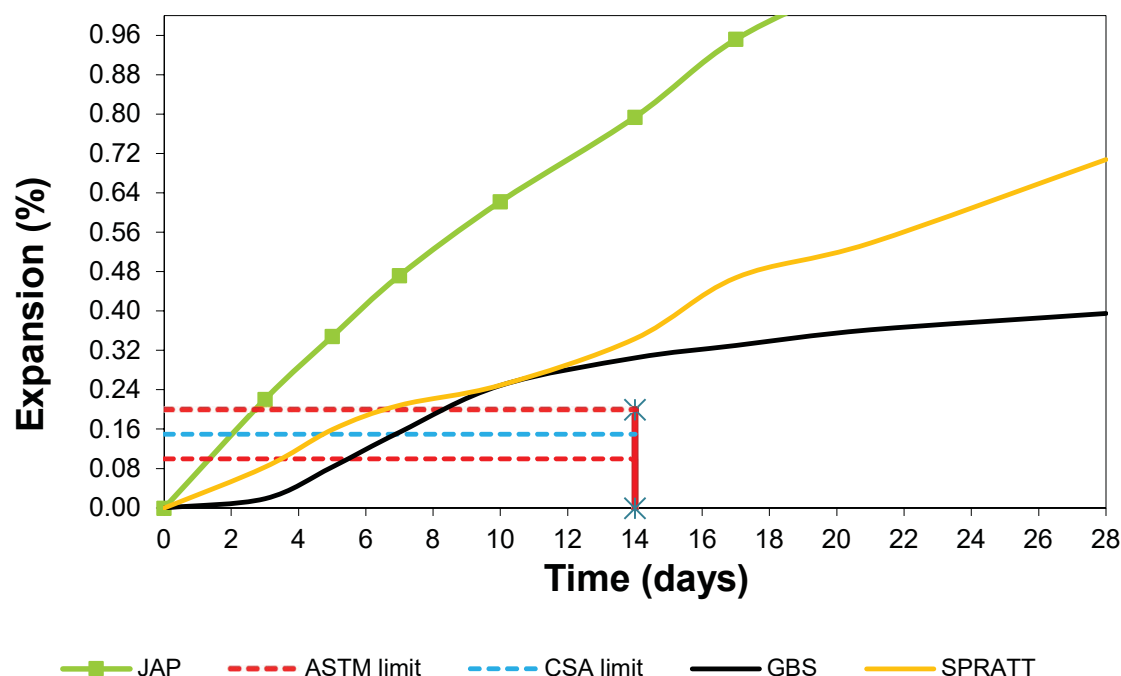


Figure 5.58. Expansion results of the accelerated mortar-bar method test at 80°C (CSA A23.2-25A) concerning the Japan aggregate.

New Zealand

The mortar bars made with aggregates NZ1 and NZ2 present low expansion while those incorporating NZ3 display high expansion. At 14 days, NZ1 and NZ2 show expansion values of 0.01% and 0.04%, respectively. And even at the end of 28 days of testing, both aggregates continue with low expansion with values reaching only 0.01% for NZ1 and 0.03% for NZ2. Regarding NZ3 aggregate, at 14 days the expansion reached 0.58% and 0.67% at the end of 28 days of testing. The expansion of NZ3 tends to stabilize with time, as can be observed in Figure 5.59.

According to all standards (ASTM C 1260, 2014; CSA A23.2-25A, 2019; CSA 23.2-27A, 2019) and recommendations (RILEM AAR-2, 2016, RILEM AAR-0, 2016), NZ1 and NZ2 aggregates are considered non-reactive. For the aggregate NZ3, the same standards and recommendations consider this aggregate potentially deleterious (expansion > 0.20% - ASTM C 1260, 2014; RILEM AAR-2, 2016, RILEM AAR-0, 2016) or extremely reactive (expansion > 0.44% - CSA A23.2-25A, 2019; CSA 23.2-27A, 2019)

The results of the accelerated mortar-bar method for the New Zealand aggregates are shown in Figure 5.59.

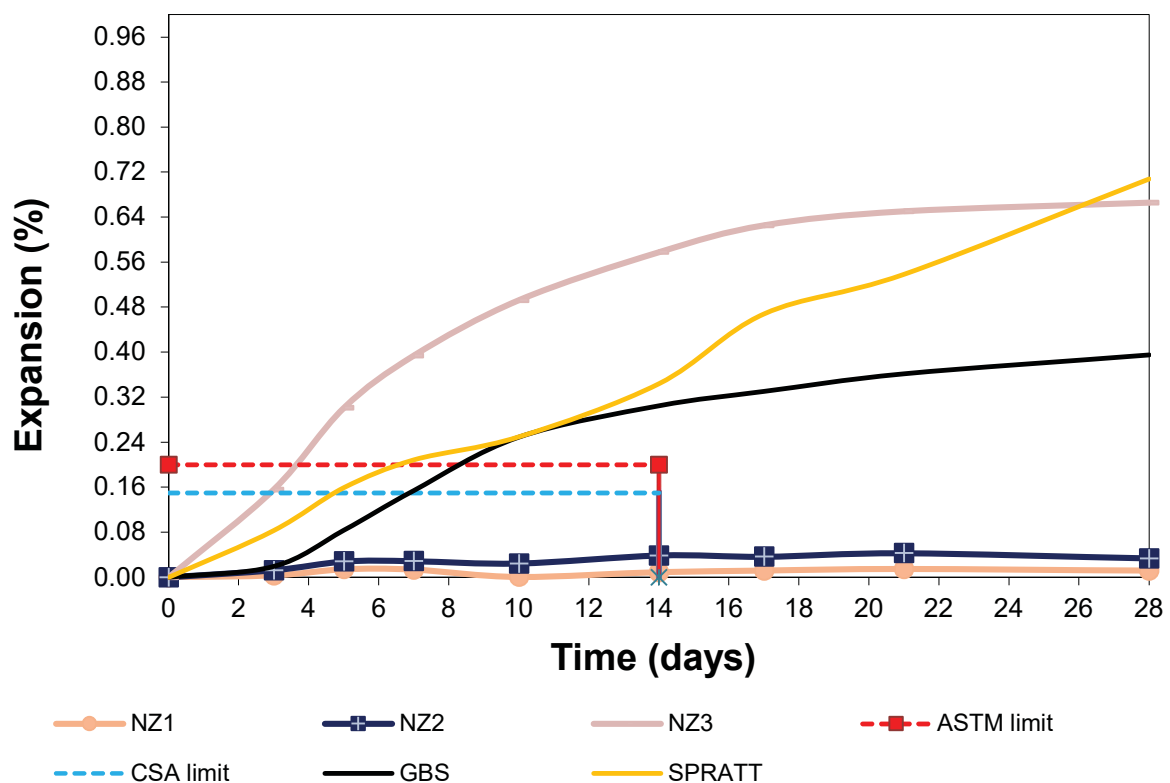


Figure 5.59. Expansion results of the accelerated mortar-bar test at 80°C (CSA A23.2-25A) concerning the New Zealand aggregates.

5.1.3.1. Post mortem mortar petrography

Thin sections were made for all the mortar bars after completion of the expansion testing to perform petrographic analysis. This analysis was done with the aid of a petrographic microscope.

Azores Archipelago (Portugal)

The Azorean mortar bars were manufactured mainly with basaltic (s.l.) crushed rocks or trachytic, in the case of TER-SM1. In general, the basaltic aggregate particles have intergranular textures with plagioclase, olivine, clinopyroxene and opaque minerals. The trachytic aggregate particles are constituted by anorthoclase, pyroxene, amphibole, plagioclase and biotite, as already presented in the 5.1 section. Some of the aggregate particles contain a small amount of honey-yellow or brown volcanic glass (Figure 5.60A). Also, some aggregate particles are more oxidized showing a darker colour. Grains of olivine, clinopyroxene and plagioclase of different sizes and amounts are visible in most mortars. The mortar with trachyte contains grains of anorthoclase and minor biotite. Some fragments of a glassy basalt are visible (Figure 5.60B) in diverse mortar samples (SMA-SM1, SMG-SM1, TER-SM1, TER-SM2, SJO-SM1, FLO-SM2) containing pyroxene and plagioclase and some are highly vesicular. In one of the mortar bars, the presence of shells in the cement matrix is noticed (Figure 5.60C).

In most of the mortar bars, there is no visible damage. There are very few cracks in the cement paste, some of them are very thin and the majority are not filled. The cracks usually cross and/or rim the aggregate particles or are only associated with pores. In one of the mortar bars using the SMA-SM2 sample, besides the cracks in the cement matrix, some cracks occur exclusively inside the aggregate particles and they are filled with yellow isotropic volcanic glass (Figure 5.60D).

The majority of the pores are empty and the rest are partly or totally filled with cement matrix, an artifact from the thin section preparation. There are pores filled with portlandite identified by the high birefringence. In the mortar bar containing the SMA-SM1 aggregate, the cement matrix is black and dense, suggesting that it is depleted of portlandite.

The mortar bar prepared with the TER-SM1 aggregate contains a crack and some pores partly filled with isotropic gel (Figure 5.60E and F). This crack connects different trachytic particles by crossing the cement paste. The gel has a texture that looks like desiccated cracks and is present in several parts of the crack.

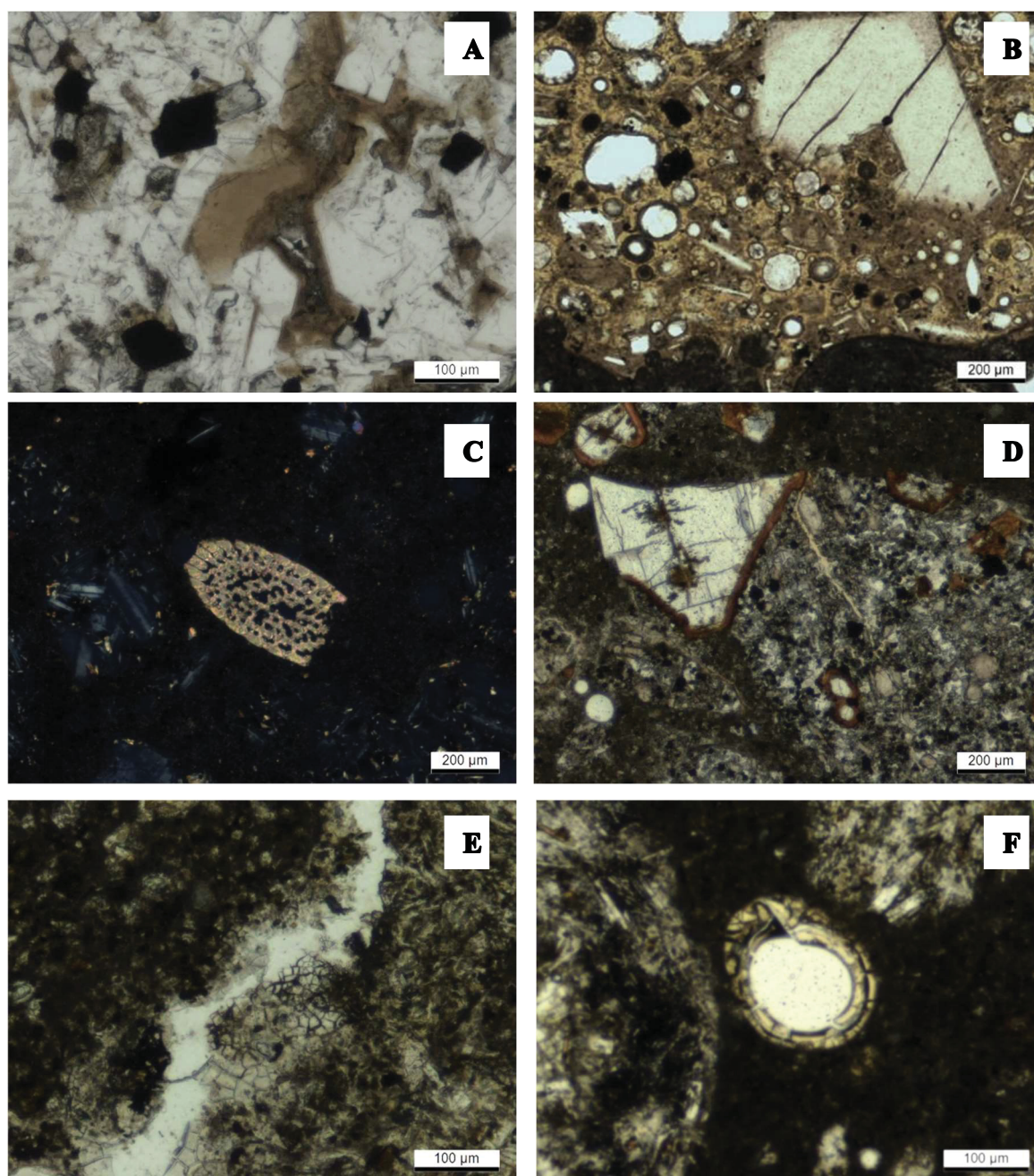


Figure 5.60. Photomicrographs of mortar bars incorporating aggregates from the Azores: C in XPL, A, B, D, E and F in PPL. A) Volcanic glass in an aggregate particle (FLO-SM1); B) Vitrophyric (glassy) basalt particle (SMG-SM1); C) Shell in the sand fraction (GRA-SM1); D) Crack inside an aggregate particle (SMA-SM2) containing volcanic glass; E) Crack with gel (TER-SM1); F) Pore partly filled with gel (TER-SM1).

Canary Islands (Spain)

The two mortar bars from the Canary Islands contain basanite crushed rocks, as described in section 5.1. In general, the aggregate particles have intergranular textures with plagioclase, iddingsitized olivine, clinopyroxene, opaque minerals, sometimes brownish volcanic glass (Figure 5.61A), and occasionally calcite. Also, in some aggregate particles, there is a darker groundmass, possibly with tachylite. Crystals in the sand fraction composed of clinopyroxene and plagioclase with different sizes are visible in both mortars and also olivine crystals are rimmed or almost completely altered to iddingsite in CANY2 aggregate. Some fragments of a glassy basalt (Figure 5.61B) are identified, especially in the mortar bar with CANY1 aggregate. These fragments contain plagioclase and opaque minerals.

In general, there are no visible cracks in the cement matrix, except at the edge of the thin section. These cracks are empty and limited only to the aggregate particles (CANY1). The majority of the pores are empty and the rest are partly or totally filled with an isotropic brownish material (Figure 5.61C). There is no visible damage in both mortar bars.

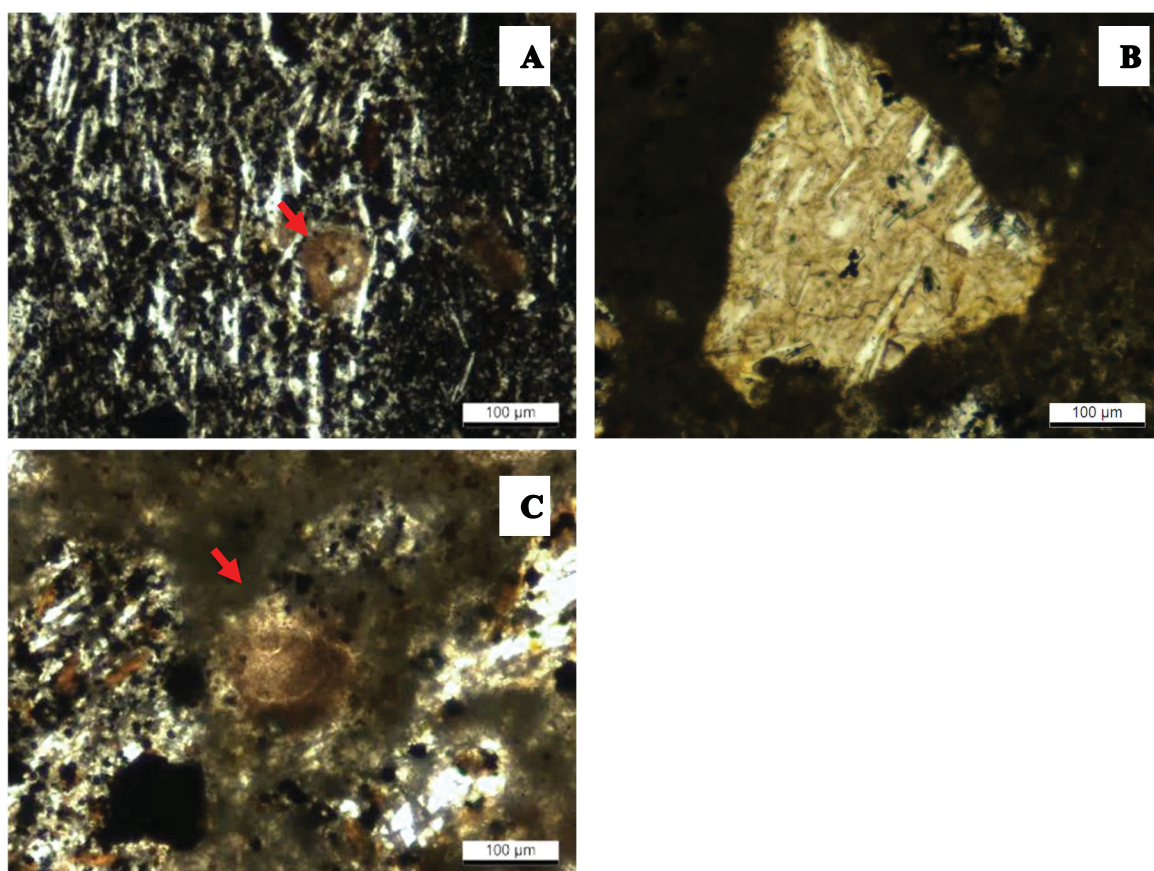


Figure 5.61. Photomicrographs of mortar bars incorporating aggregates from the Canary Islands. Photo D in XPL. Photos A, B and C in PPL. A) Volcanic glass in an aggregate particle (CANY2); B) Glassy basalt particle (CANY1); C) Pore filled with isotropic brownish material (CANY1).

Hawaiian Islands (USA)

The Hawaiian mortar bars are manufactured with basaltic crushed rocks. In general, the basaltic aggregate particles have intergranular, intersertal and subophitic textures with plagioclase, olivine (some with iddingsite), clinopyroxene, opaque minerals and brownish volcanic glass either filling the interstices of the rock or filling vesicles or both. Grains of olivine, clinopyroxene and plagioclase of different sizes and proportions are scattered throughout the cement matrix. Orthopyroxene and biotite grains are also found but only in the mortars containing aggregates HW5/HW6 and HW4, respectively. Some aggregate particles present a variolitic texture, and several particles have plagioclase crystals set in a tachylite dark groundmass. Some mortars (HW4 and HW5/HW6) contain minor fragments of glassy basalt (Figure 5.62A) with plagioclase and sometimes olivine.

In three of the mortars (HW2, HW4 and HW4 sand), the presence of cracks is rare, either in the cement paste or in the aggregate particles. However, the mortar containing HW4 sand has more cracks than the other two and they are scattered in the cement matrix. These cracks are usually thin, empty and not long. Most pores are empty but others are lined with an isotropic brownish gel.

The rest of the mortars present several cracks distributed throughout the cement matrix and in the aggregate particles. Some of them are filled with an isotropic brownish gel. Some cracks are long and mainly surround several aggregates, showing debonding of the particles, and cross other particles (Figure 5.62B, C and D), also connecting with some pores. There are cases where the gel occurs inside the aggregate particles but also fills the cracks in the interfaces (Figure 5.62E). Gel also occurs in cracks crossing the aggregate particles and then extending into the cement matrix (Figure 5.62F).

Regarding the pores, these can be: (1) empty; (2) lined with brownish gel; (3) filled with what seems to be cement matrix and lined with brownish gel; (4) partly filled with what seems to be cement matrix and brownish gel; (5) filled with gel.

There is visible damage in most mortar bars. There is evidence for the presence of ASR gel in the majority of the mortar bars that seem to be starting in the basaltic aggregate particles.

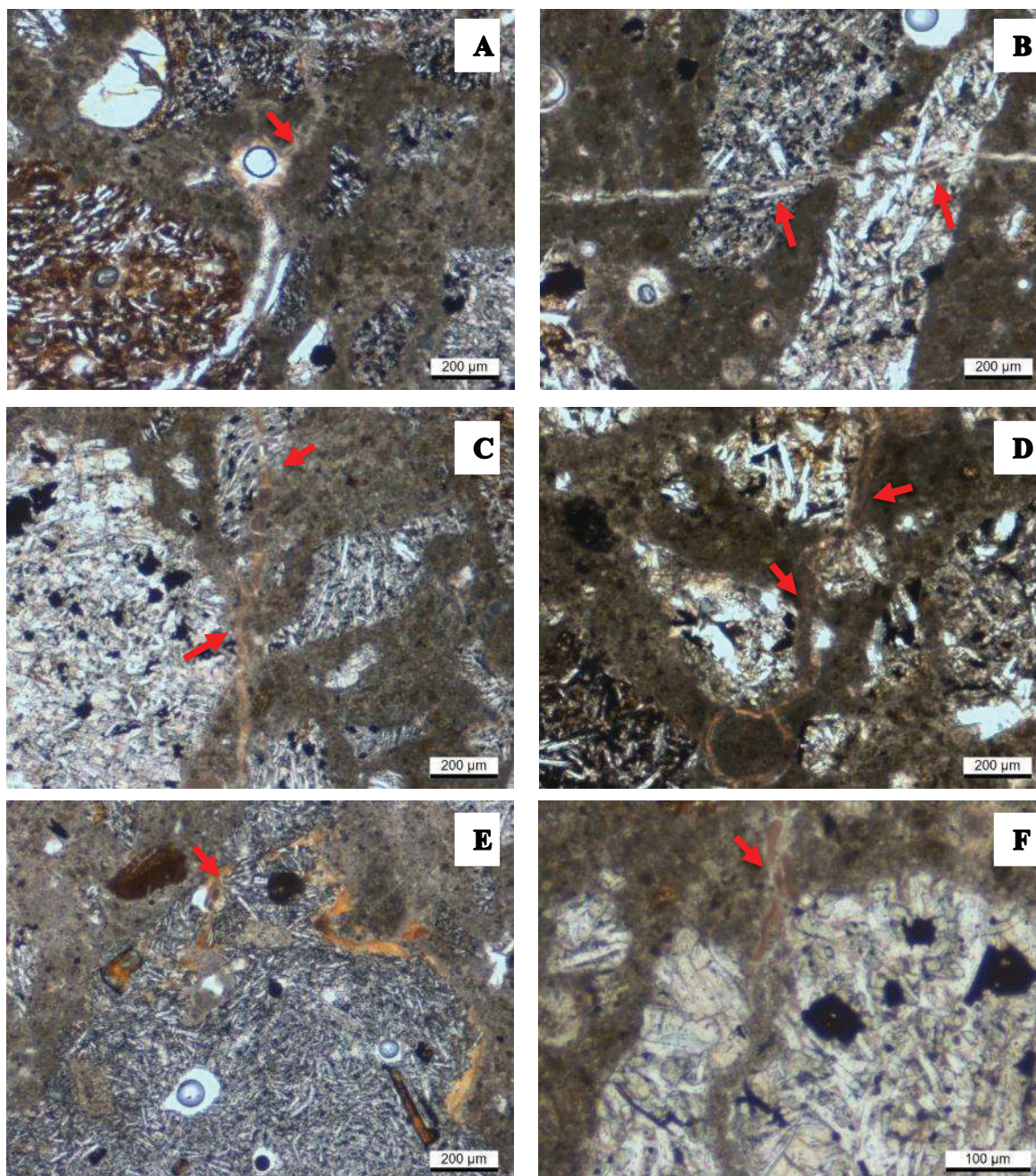


Figure 5.62. Photomicrographs of mortar bars incorporating Hawaiian aggregates. All photos are in PPL. A) Crack with brownish gel crossing two aggregate particles and one pore (HW1); B) Crack with brownish gel crossing two aggregate particles and the cement paste (HW3); C) Crack with brownish gel crossing one particle and partially surrounding other two particles (HW5/6); D) Crack with brownish gel crossing one particle and surrounding other two particles (HW7); E) Gel inside an aggregate particle and lining it (HW5/6); F) Crack starting in an aggregate particle, filled with brownish gel, and extending into the cement paste (HW5/6).

Iceland

The Icelandic mortar bars contain crushed basaltic aggregate or gravels with different lithologies, the latter representing the majority of the samples tested. The aggregate particles in the mortars are mainly of basaltic composition with different degrees of alteration. In general, they have intergranular, intersertal and/or subophitic textures with plagioclase, olivine (some with iddingsite), clinopyroxene, opaque minerals and fresh or altered volcanic glass. The presence of chlorite is common in the altered basaltic aggregate particles, in some cases filling the amygdales together with zeolites. Also, some basaltic aggregate particles show plagioclase set in a tachylite dark groundmass. Glassy basaltic particles are also visible in most of the mortar samples. The other lithologies observed include rhyolite and dacite. The rhyolite particles are mainly aphyric containing silica minerals, feldspars and devitrified volcanic glass. Dacite contains mainly phenocrysts of plagioclase and quartz. Also, some aggregate particles contain microcrystalline quartz, which is the case for ICL1 gravel.

In ICL1 coarse sand, several aggregate particles are partly outlined by brownish gel (Figure 5.63A) and several cracks in the cement paste are filled with gel. Some aggregate particles are cracked and filled with gel. These aggregates include basaltic particles (Figure 5.63B) and microcrystalline quartz (Figure 5.63C). Volcanic glass occurs in a basaltic aggregate particle (Figure 5.63D and E). The air voids are filled or lined by brownish material (Figure 5.63F).

ICL1 fine sand mortar is similar to the ICL1 coarse sand mortar. There are several aggregate particles partly outlined by brownish gel, even more abundant than for the ICL1 coarse sand. The cracks in the cement matrix are partly or totally filled with gel; they connect several aggregate particles and either surround or cross them. Cracks are associated with: the existence of volcanic glass (Figure 5.64A), starting inside the aggregate and extending into the cement paste (Figure 5.64B); glassy basalt (Figure 5.64C); lighter colour aggregate particle (Figure 5.64D). The cracks can also be confined to the aggregate particles, as in the dark basalt in Figure 5.64E. Like in ICL1 coarse sand, the gel filling the cracks is sometimes dark and dull (Figure 5.64F). The air voids are filled by brownish material.

In ICL1 aggregate, there are several particles filled with gel (Figure 5.65A, B, C, D) but there are less cracks in the cement matrix with gel when compared to the ICL1 coarse and fine sand material. In this aggregate, the voids are partly or totally filled by ASR gel.

In ICL2 aggregate, there are very few cracks in the cement matrix and within the aggregate particles (Figure 5.65E). The presence of gel is restricted to some aggregate particles and some of the air voids (Figure 5.65F).

Mortar bars made with ICL3 aggregate and ICL3 sand have very few cracks (Figure 5.66A). The majority of the air voids are empty and some are partly filled with cement matrix from the thin section preparation.

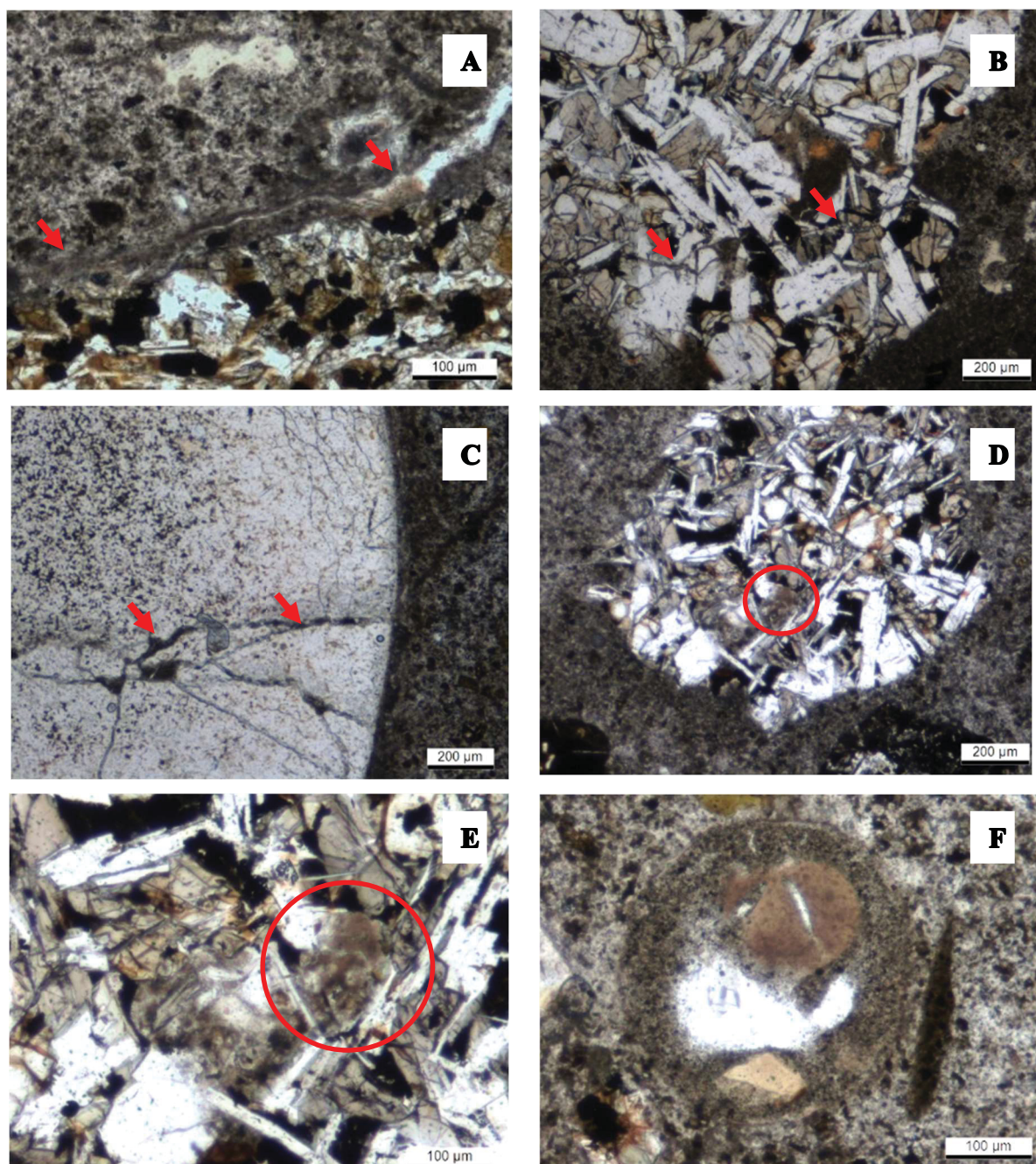


Figure 5.63. Photomicrographs of mortar bars made with ICL1 coarse sand. All photos are in PPL. A)

Crack outlining an aggregate particle with brownish gel; B) Crack within the basaltic aggregate particle; C) Crack within a microcrystalline quartz particle; D) Volcanic glass in a basaltic aggregate particle; E) Detail of the volcanic glass inside a basaltic aggregate particle; F) Air void partly filled with brownish material.

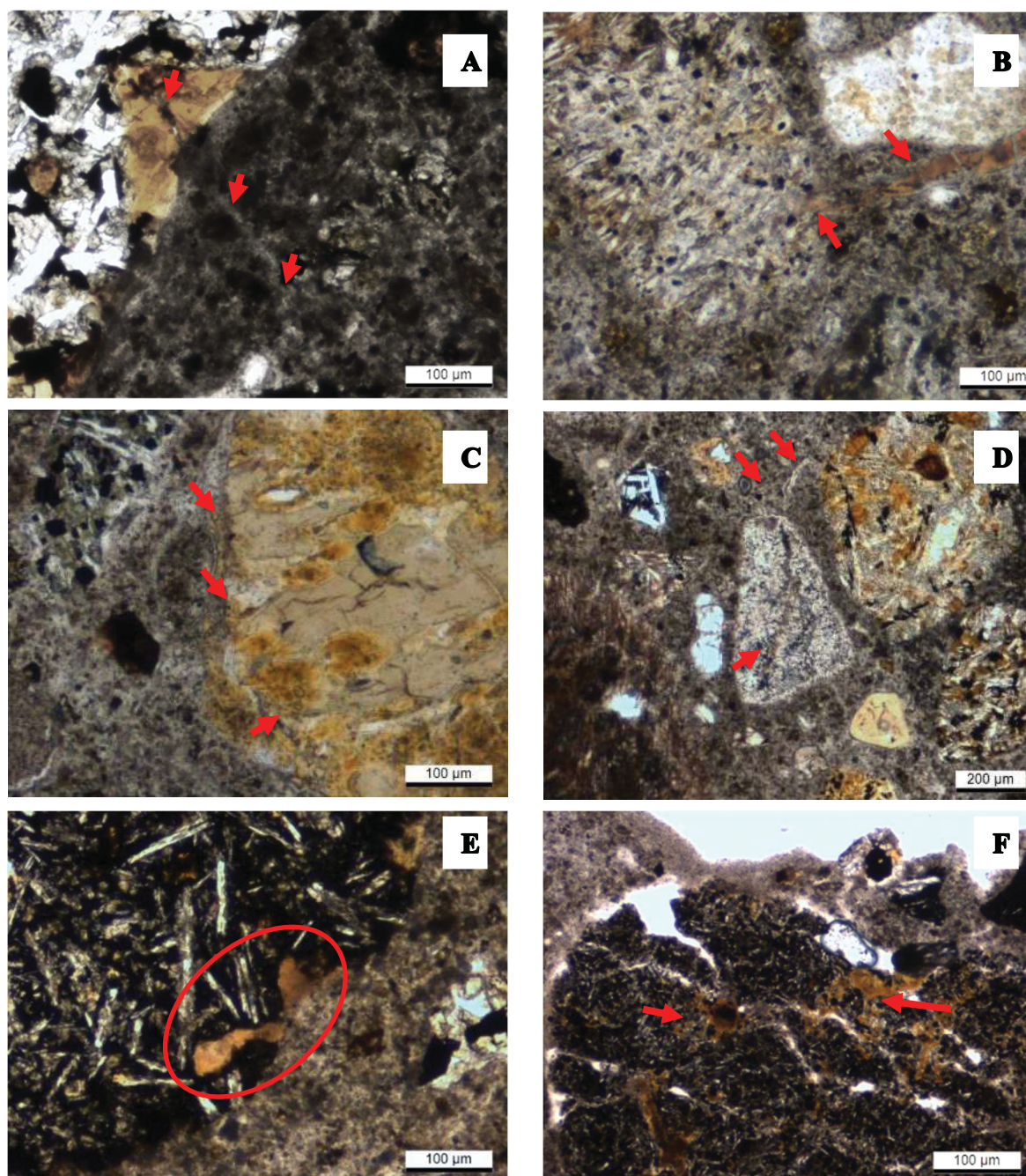


Figure 5.64. Photomicrographs of mortar bar incorporating ICL1 fine sand. All photos are in PPL. . A) Crack with brownish gel associated with the volcanic glass within the basaltic aggregate particle and extending into the cement matrix; B) Crack with brownish gel both in a basaltic aggregate particle and in the cement matrix; C) Crack with brownish gel both in a glassy basalt particle and in the cement matrix; D) Crack with brownish gel crossing a rhyolite particle and the cement matrix; E) Gel within a basaltic aggregate particle; F) basaltic aggregate particle containing cracks with dull, dark brownish gel.

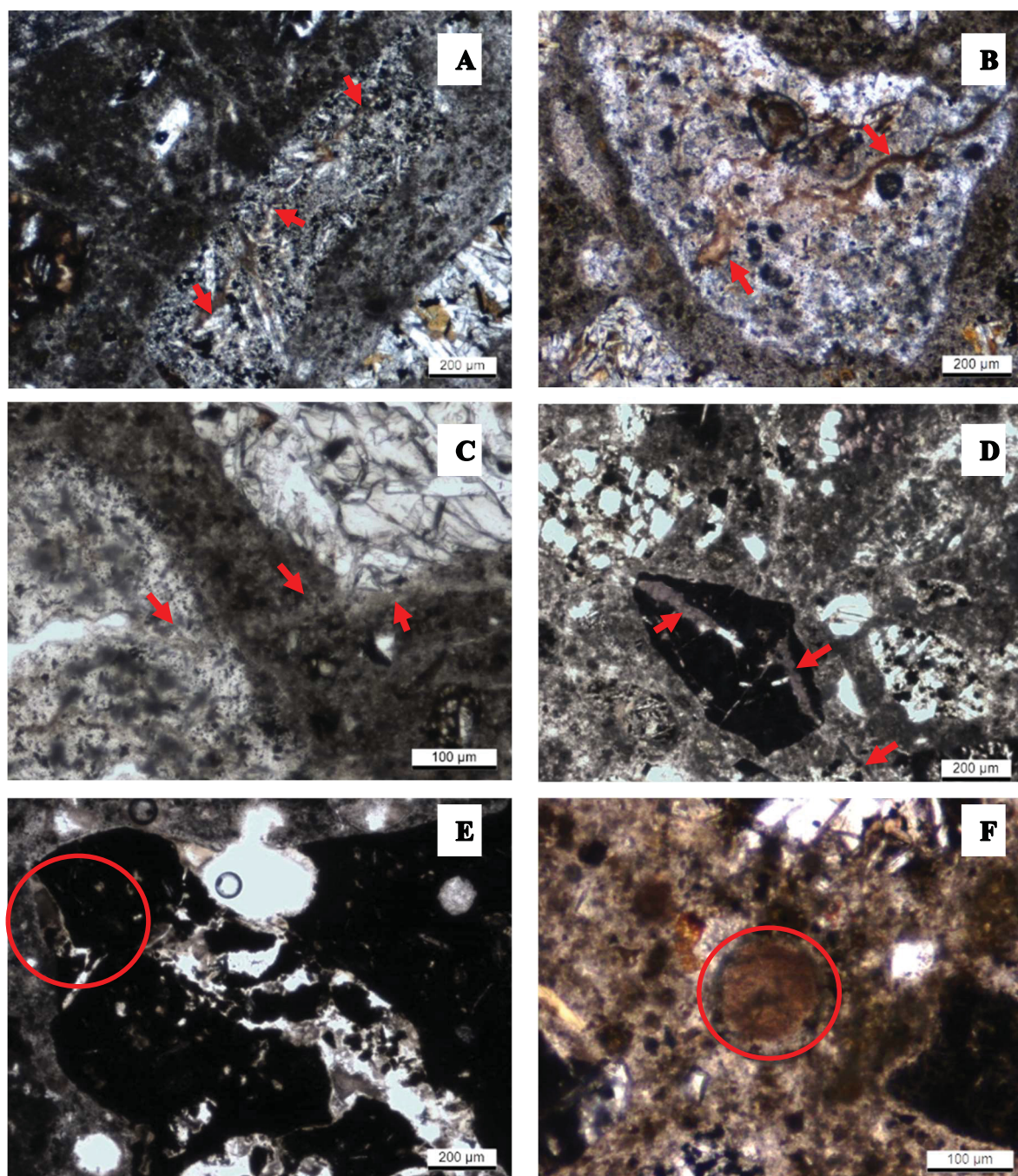


Figure 5.65. Photomicrographs of mortar bars made with ICL1 and ICL2 aggregates. All photos are in PPL. A) Crack with brownish gel within the basalt particle (ICL1); B) Crack with brownish gel within a rhyolitic aggregate particle (ICL1); C) Crack with brownish gel crossing a rhyolite particle and the cement matrix (ICL1); D) Crack with brownish gel in a dark basaltic particle and in the cement matrix (ICL1); E) Gel within a basaltic aggregate particle (ICL2); F) Void filled with brownish material (ICL2).

ICL4 aggregate mortar presents several cracks in the cement matrix and within the aggregate particles. The rhyolite particles seem to be causing the majority of the gel produced, although some basalt particles are also causing ASR (Figure 5.66B and C). In several examples, the cracks extend into the cement paste and gel also occurs in the interfacial zone between the aggregate particles and the cement paste. The cracks in the cement paste seem to form a network, a large part being filled or partly filled with gel. The air voids are mainly lined or filled by gel, in some cases, ettringite is also present (Figure 5.66D).

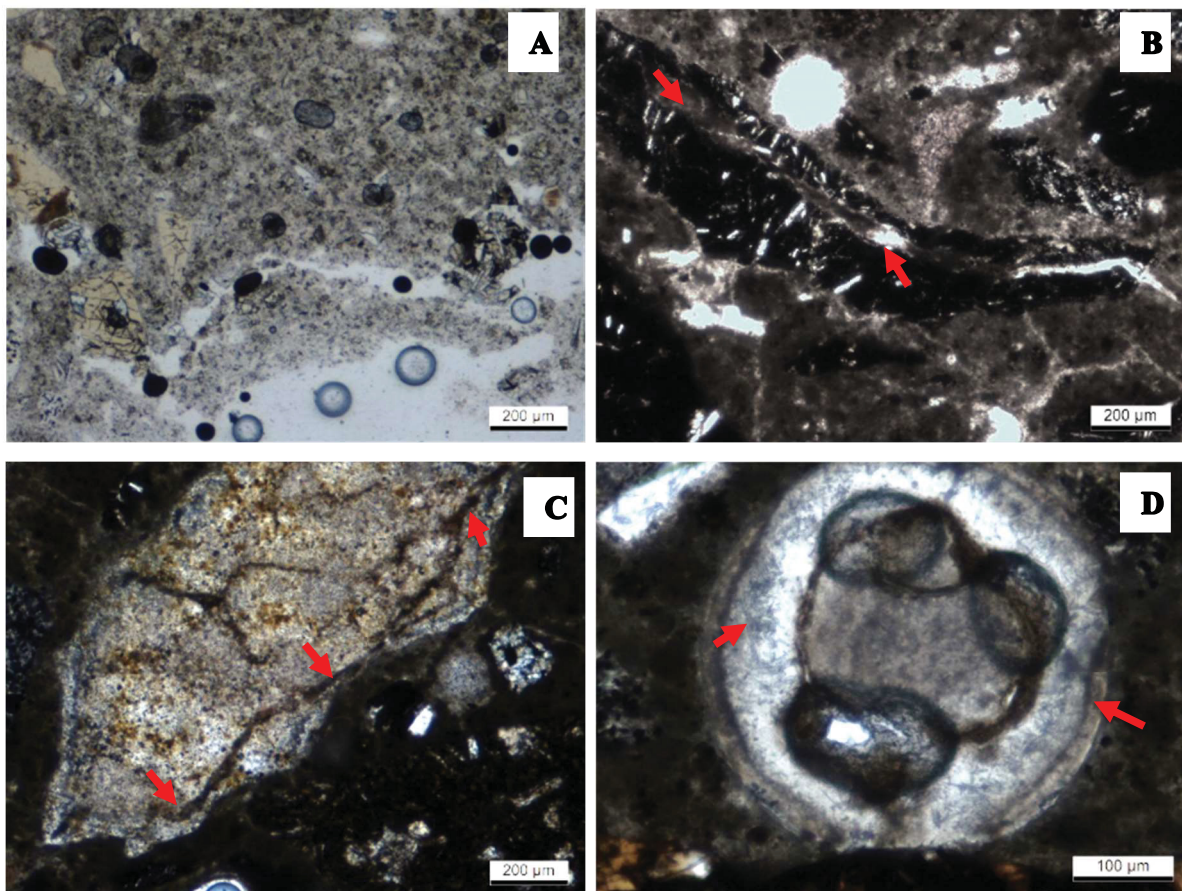


Figure 5.66. Photomicrographs of mortar bars incorporating ICL3 sand and ICL4 aggregate. All photos are in PPL. A) Empty crack at the edge of the thin section caused by the thin section preparation (ICL3 sand); B) Brownish gel in a crack within a dark basaltic particle that extends into the cement paste (ICL4); C) Brownish gel in cracks inside a rhyolite particle that extends into the cement paste (ICL4); D) Void with ettringite and lined by gel (ICL4).

The mortar made with ICL4 sand has several large cracks in the cement paste (Figure 5.67A) and in many aggregate particles, although most of them are empty. The presence of gel was only observed outlining partly three aggregate particles (Figure 5.67B). Occasionally, some voids contain gel.

GBS sand is formed by the same type of aggregate particles and textures as the other gravels where basalt represents the main fraction. There are some cracks in the cement paste, the majority of them being thin. The presence of gel is noticed in some sections. One example is observed in a rhyolite particle where gel extends into the paste and outlines partially a basaltic aggregate (Figure 5.67C). Another example comes from a basaltic particle that continues into the cement paste outlining different particles (Figure 5.67D).

There is visible damage in half of the mortar bars examined. There is evidence of the presence of ASR gel in the other half of the mortar bars; the reaction seems to be associated with the rhyolitic particles but also with the basaltic aggregate particles.

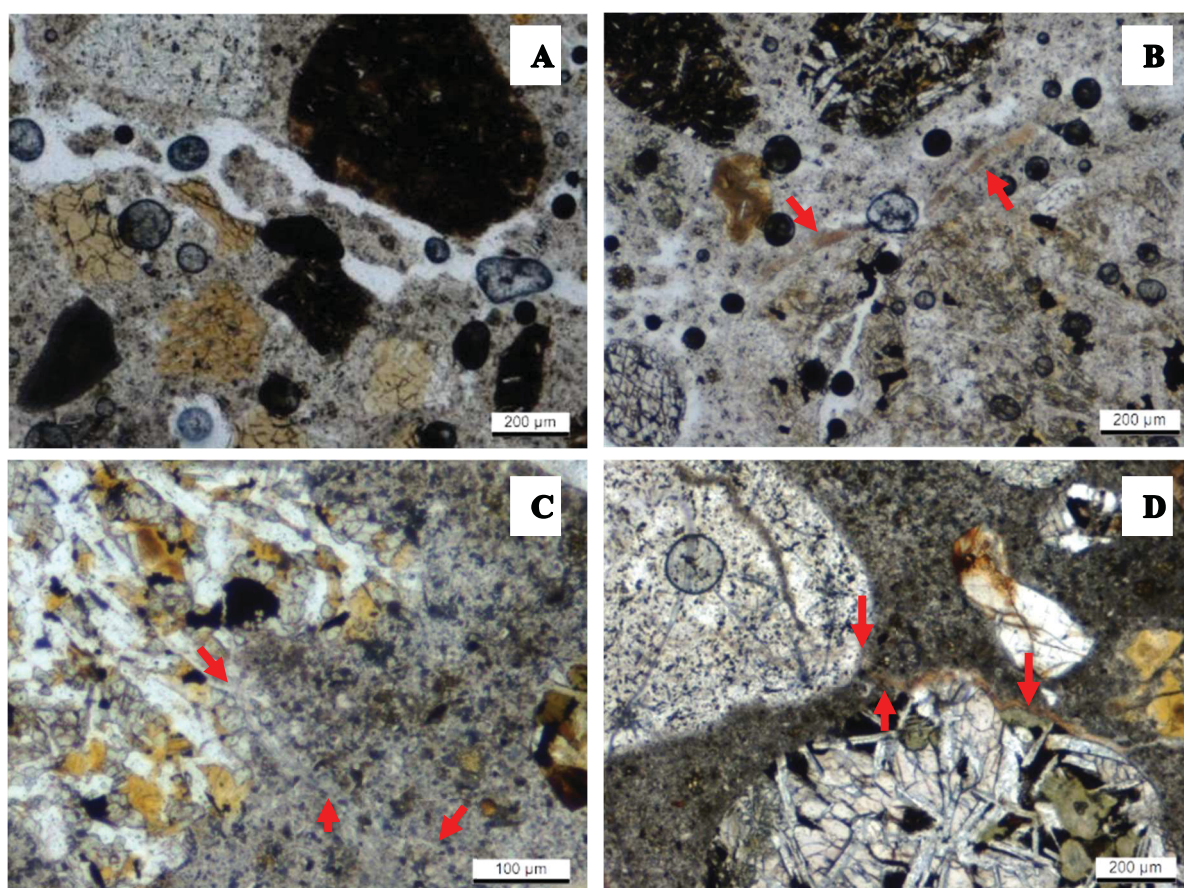


Figure 5.67. Photomicrographs of mortar bar incorporating ICL4 sand and GBS sand. All photos are in PPL. A) Large cracks in the cement paste (ICL4 sand); B) Brownish gel lining an aggregate particle (ICL4 sand); C) Brownish gel within a basalt particle that extends into the cement paste (GBS sand); D) Brownish gel in a crack within a rhyolitic particle and that extends into the cement paste (GBS sand).

Japan

The Japan (JAP) mortar bars contain andesitic crushed rock. In general, the andesite has an intergranular texture with plagioclase, clinopyroxene and orthopyroxene, some iddingsitized olivine, opaque minerals and silica minerals. In addition, crystals of plagioclase and pyroxene of different sizes are visible scattered in the cement matrix.

The mortar shows several cracks, some are large and long and others are thin, but both run through the cement matrix and cross various particles. Some of the cracks contain an isotropic brownish material that connects and crosses several aggregate particles (Figure 5.68A). Sometimes the brownish material remains only in the cracks inside the aggregate particles despite the crack continuity through the cement matrix (Figure 5.68B). This happens in a quite number of aggregate particles. There are also a few cracks, some quite large, that cross the aggregate particles and the cement matrix but they are not filled with any gel (Figure 5.68C).

A part of the pores is partly filled with the same brownish material as the cracks (Figure 5.68D), while others seem to be partly filled with needle crystals of ettringite (Figure 5.68E). Isotropic beige gel and a mix of amorphous and crystalline gel are also observed (Figure 5.68F). Most pores are connected by cracks with aggregate particles or with other pores.

There is clear evidence that the andesite aggregate is responsible for the number of cracks and the presence of the isotropic beige and brownish material. It is evident that an ongoing ASR is happening due to the andesite aggregates.

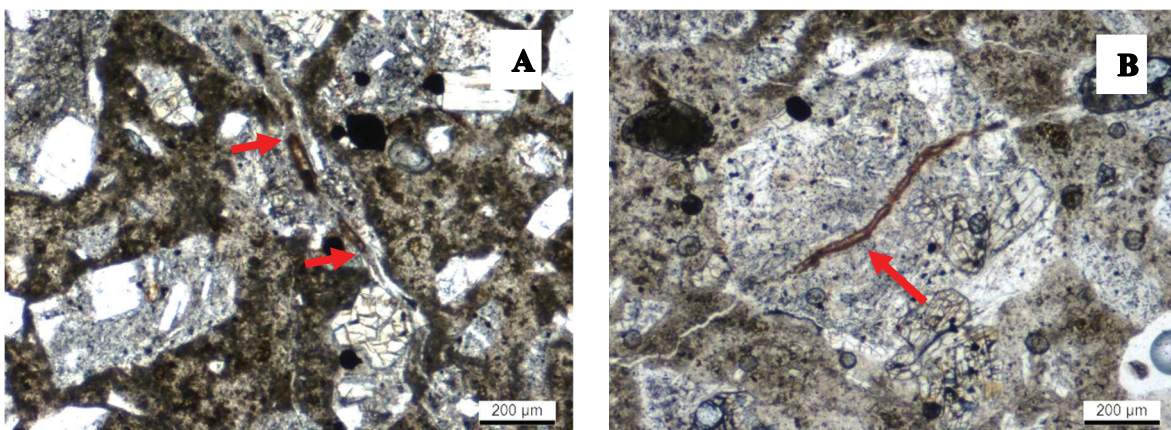


Figure 5.68. Photomicrographs of mortar bar incorporating JAP aggregate. All photos are in PPL. A) Crack crossing aggregate particles and the cement paste, filled with an isotropic brownish material; B) Brownish material restricted to a crack inside an aggregate particle.

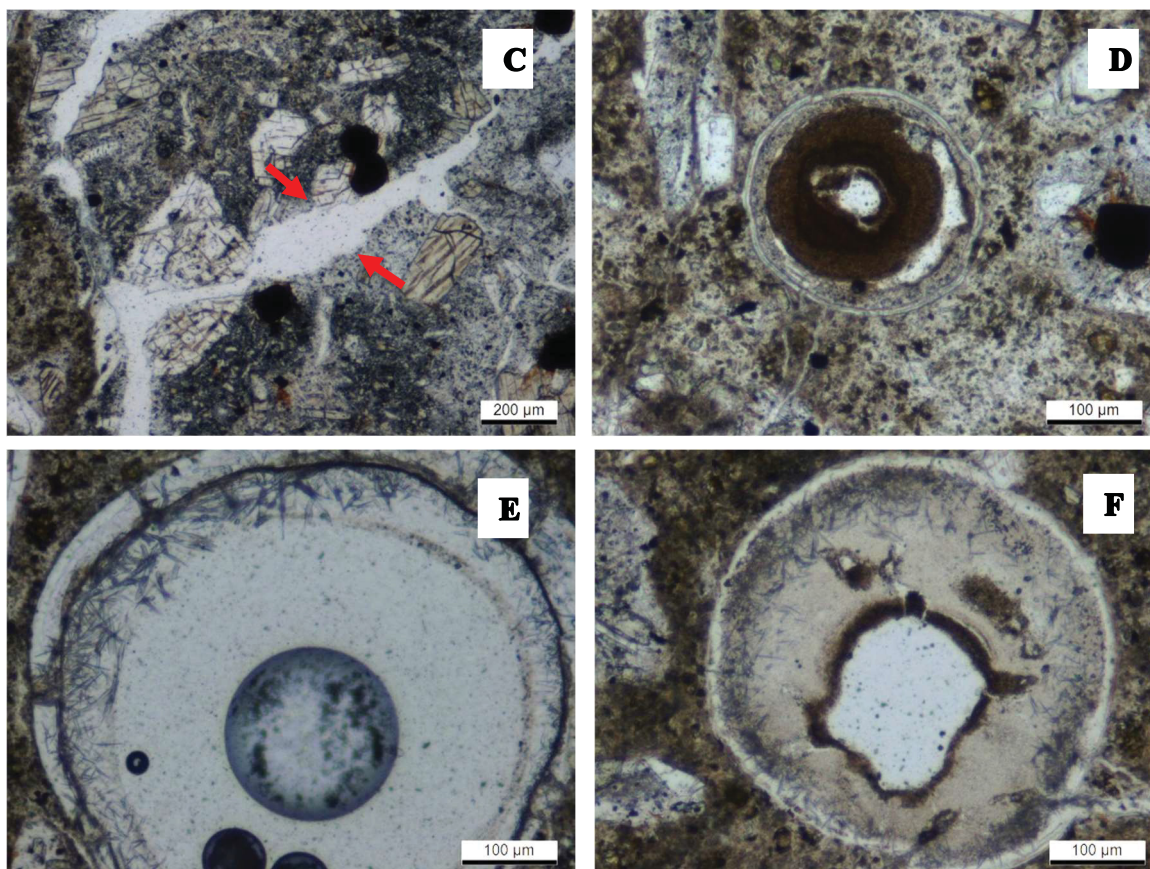


Figure 5.68 (continued). Photomicrographs of mortar bar incorporating JAP aggregate. All photos are in PPL. C) Huge empty crack in an aggregate particle; D) Pore partly filled by brownish material and rimmed by colourless gel; E) Pore partly lined with gel and needle crystals of ettringite; F) Pore partly filled with gel and crystals of ettringite.

New Zealand

The New Zealand mortar bars contain basanite (NZ1) and basaltic (NZ2 and NZ3) crushed rocks. The basanite has intersertal textures with iddingsitized olivine, plagioclase, clinopyroxene, opaque minerals, lighter brown to dark brown volcanic glass (Figure 5.69A), altered volcanic glass, chlorite and zeolites. On the other hand, the basalt presents intergranular to intersertal textures with plagioclase, olivine (some with iddingsite), clinopyroxene, opaque minerals and some brown volcanic glass. Also, some aggregate particles appear more oxidized showing a darker colour and others show a variolitic texture (NZ1). Crystals mainly of olivine (NZ1, NZ2, NZ3), plagioclase (NZ1, NZ2) (Figure 5.69B) and clinopyroxene (NZ2, NZ3) appear scattered in the cement matrix with different sizes and in different proportions. Also, fragments of glassy basalt (Figure 5.69C) occur in the mortar with

NZ3 aggregate. These fragments are constituted essentially by plagioclase and sometimes by clinopyroxene and some are vesicular.

There are only very few cracks in the cement matrix of mortars NZ1 and NZ2. There is limited cracking inside the aggregate particles and only a few of those cracks are filled with a yellow material (NZ1) (Figure 5.69D) that is not completely isotropic and resembles altered volcanic glass. The pores are empty.

In the case of the mortar with NZ3 aggregate, there are several cracks scattered all over the cement paste. Some of the cracks are small and thin, others are larger and longer. Most of the cracks are not filled, but some cracks are filled with an isotropic brownish gel that rims and crosses aggregate particles (Figure 5.69E). In some cases, the isotropic brownish gel is only restricted to the cracks inside the aggregate particles, either if the crack continues to the cement matrix or not (Figure 5.69F). Most of the pores are empty and not connected by cracks with other pores and aggregate particles. The ones that are not empty are lined or partly or totally filled with gel and acicular crystals.

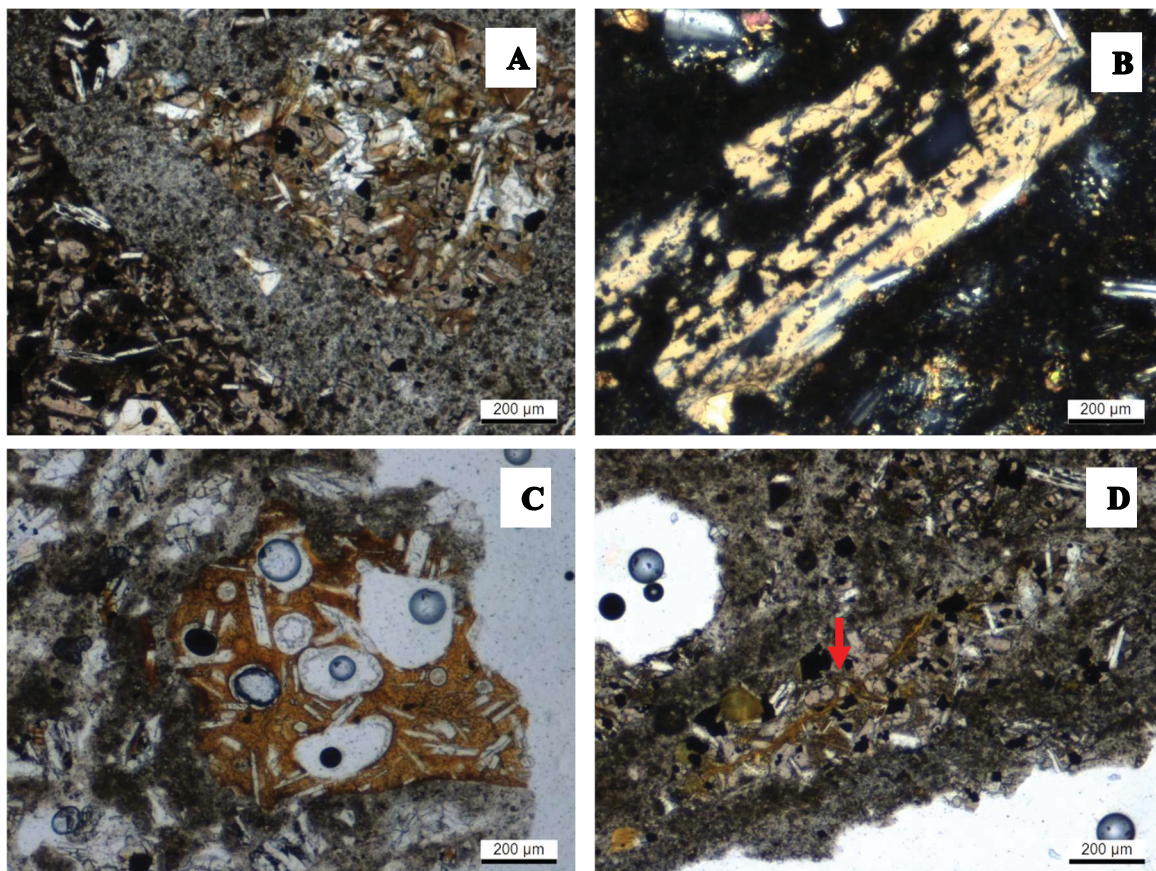


Figure 5.69. Photomicrographs of mortar bars incorporating New Zealand aggregates: B in XPL; A, C, D, E and F in PPL. A) Volcanic glass in two aggregate particles with different shades of brown colour (NZ1); B) Plagioclase crystal particle in the finer fraction of the aggregates (NZ2); C) Glassy basaltic particle (NZ3); D) Aggregate particle cut by a crack filled with a yellow material (NZ1).

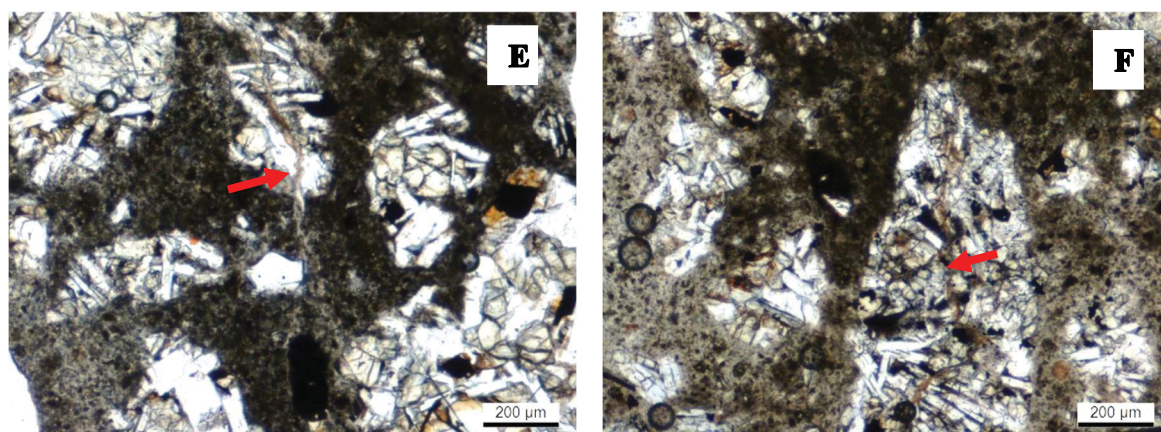


Figure 5.69 (continued). Photomicrographs of mortar bars incorporating New Zealand aggregates: All in PPL. E) Crack crossing an aggregate particle filled with isotropic brownish gel (NZ3); F) Yellowish gel restricted to a crack inside an aggregate particle (NZ3).

5.1.4. Concrete studies

5.1.4.1. Expansion tests - Concrete prism test at 38°C (CSA A23.2-14A, 2015)

Several concrete prism tests were performed for the present study. Thirty mixes were prepared at Université Laval, in Québec, Canada. For the Azorean aggregates, thirteen mixes were made at the National Laboratory for Civil Engineering (LNEC), in Lisbon, Portugal within the scope of the ReAVA (2012-2014) and IMPROVE research projects, except for the aggregate from Corvo Island (CRV) that was prepared at Université Laval within the present study. The Spratt and the GBS sand were used as references for each graphic.

The characteristics of the concrete are the same as presented in Table 4.13 in chapter 4. The CPT method is described by the CSA A23.2-14A (2015), ASTM C 1293 (2020) and RILEM AAR-3 (2016) but the limits are provided by the CSA Standard Practice A23.2-27A (2019), ASTM C 1778 (2020) and RILEM AAR-0 (2016).

Azores Archipelago (Portugal)

The results obtained after one year of testing show the following expansion values for the different aggregates: SMA-SM1 = 0.022%, SMA-SM2 = 0.016%, SMG-SM1 = 0.017%, SMG-SM2 = 0.037%, SMG-SM3 = 0.016%, TER-SM1 = 0.021%, TER-SM2 = 0.025%, GRA-SM1 = 0.027%, SJO-SM1 = 0.030%, FAI-SM1 = 0.019%, FLO-SM1 = 0.007% and FLO-SM2 = 0.007%). All the aggregates display expansion lower than the limit indicated by the standards. However, SMG-SM2 aggregate expansion is very close to the limit value of 0.04% for one year of testing, the threshold between non-reactive and moderately reactive, as stated by the American and Canadian standards. The testing for all aggregates was extended until week

104; during this time, the expansion continues to increase with time. Several aggregates actually pass the limit of 0.04%, but not necessarily by a huge margin: SMA-SM1 (0.048%), SMA-SM2 (0.040%), SMG-SM2 (0.064%), TER-SM1 (0.043%), TER-SM2 (0.055%), GRA-SM1 (0.053%), SJO-SM1 (0.055%), PIC-SM1 (0.056%) and FAI-SM1 (0.043%).

According to the different standards and recommendations, after one year of testing, all aggregates display expansion lower than the limit values of 0.04% (ASTM C 1778, 2020; CSA 23.2-27A, 2019) and 0.05% (RILEM AAR-0, 2016) which classifies the aggregates as non-reactive.

The results of the CPT for CRV aggregate present very low expansion with values reaching 0.009% at the end of one year of testing. There is a small increase in expansion with a tendency for stabilization with time. According to the limits of expansion indicated in ASTM C 1778, (2014) for the American standard in the CSA 23.2-27A (2019) for the Canadian standard CSA A23.2-14A (2015) and in the recommendations of RILEM AAR-0 (2016), this aggregate is considered non-reactive. The results of the concrete prism test for the Azorean aggregates are presented in Figure 5.70.

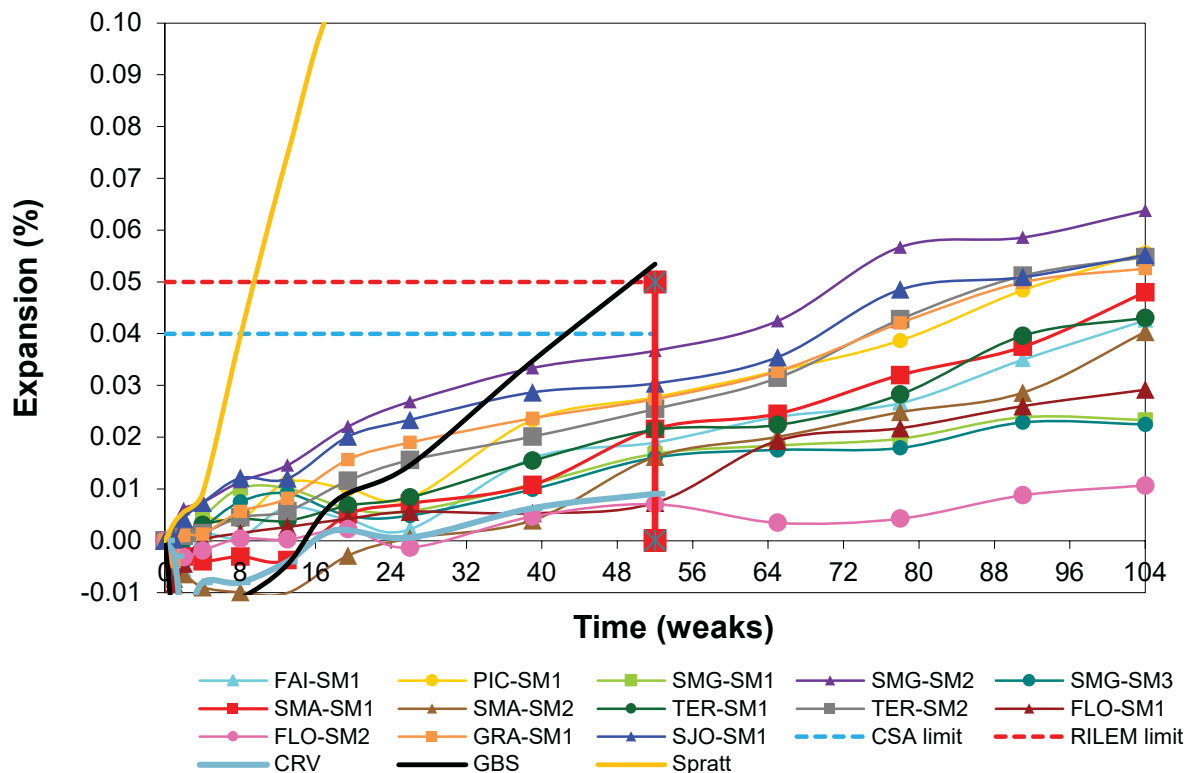


Figure 5.70. Expansion results of the CPT method test at 38°C concerning the Azorean aggregates (RILEM AAR-3; CSA A23.2-14A).

Canary Islands (Spain)

The test prisms incorporating the two aggregates CANY1 and CANY2 show low expansion. At the end of one year of testing, the expansion values are 0.012% for CANY1 and 0.024% for CANY2. There is a low increase in the rate of expansion with a tendency for stabilization after week 39.

The results obtained for these two aggregates classify them as non-reactive, in accordance with the expansion limits for the American and Canadian standards ($< 0.04\%$) and for the RILEM recommendations ($< 0.05\%$).

The results of the CPT method for the aggregates from Canary are shown in Figure 5.71.

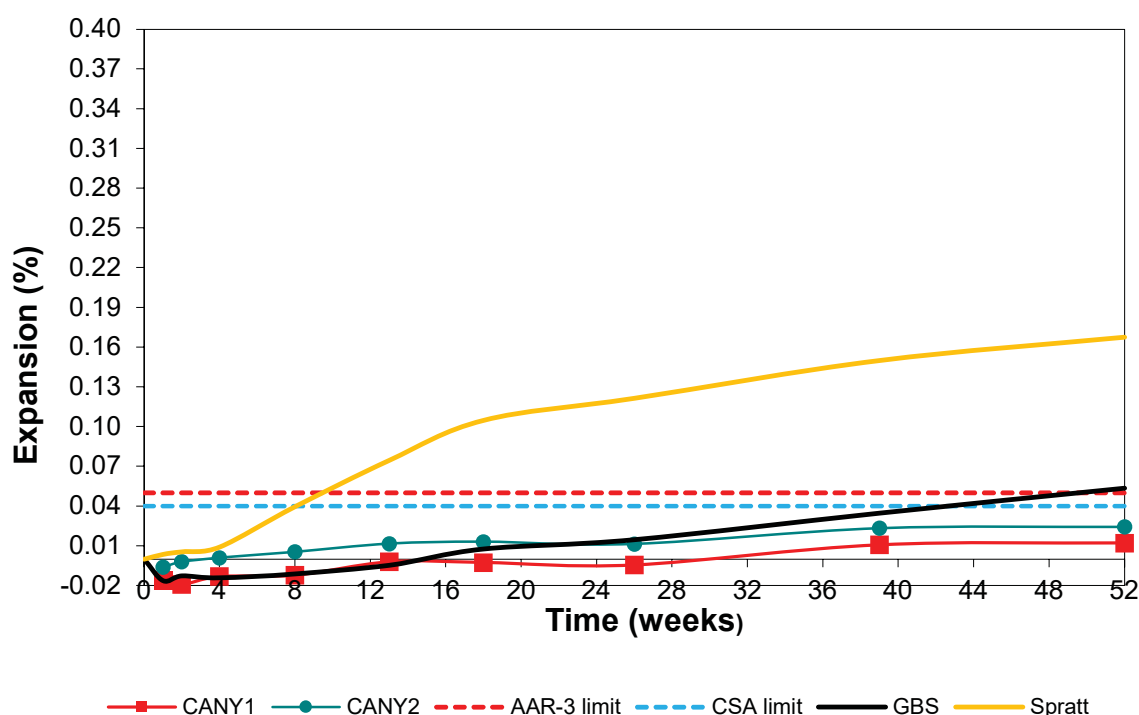


Figure 5.71. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the Canary aggregates.

Hawaiian Islands (USA)

Most of the test prisms made with the Hawaiian aggregates show low expansion and only one set of test prisms presents high expansion. At the end of one year of testing, the expansion values of the majority of the aggregates range from 0.006% to 0.027% (HW1 – 0.018%; HW2 – 0.011%; HW3 – 0.027%; HW4 – 0.019%, HW4 sand + HP – 0.006%; HW5 and HW6- 0.021%; HW7 – 0.011%; HW7 CA+FA – 0.014%). The aggregates started to show some

stabilization around week 39. Regarding the aggregate HW7 sand + HP (non-reactive high purity limestone coarse aggregate), the expansion took a leap between the 8th (0.003) and 13th (0.137) week of testing. The expansion continued to increase until the end of the testing reaching an expansion value of 0.319%. Though, there is still an increasing trend of the expansion from aggregate HW7 sand.

The results obtained show that most aggregates are considered non-reactive in accordance with the expansion limits indicated in the American and Canadian standards ($< 0.04\%$) and in the RILEM recommendations ($< 0.05\%$). As for the HW7 sand aggregate, it is considered very highly reactive for both standards and reactive for the RILEM recommendation.

The results for the CPT method for the Hawaiian aggregates are shown in Figure 5.72.

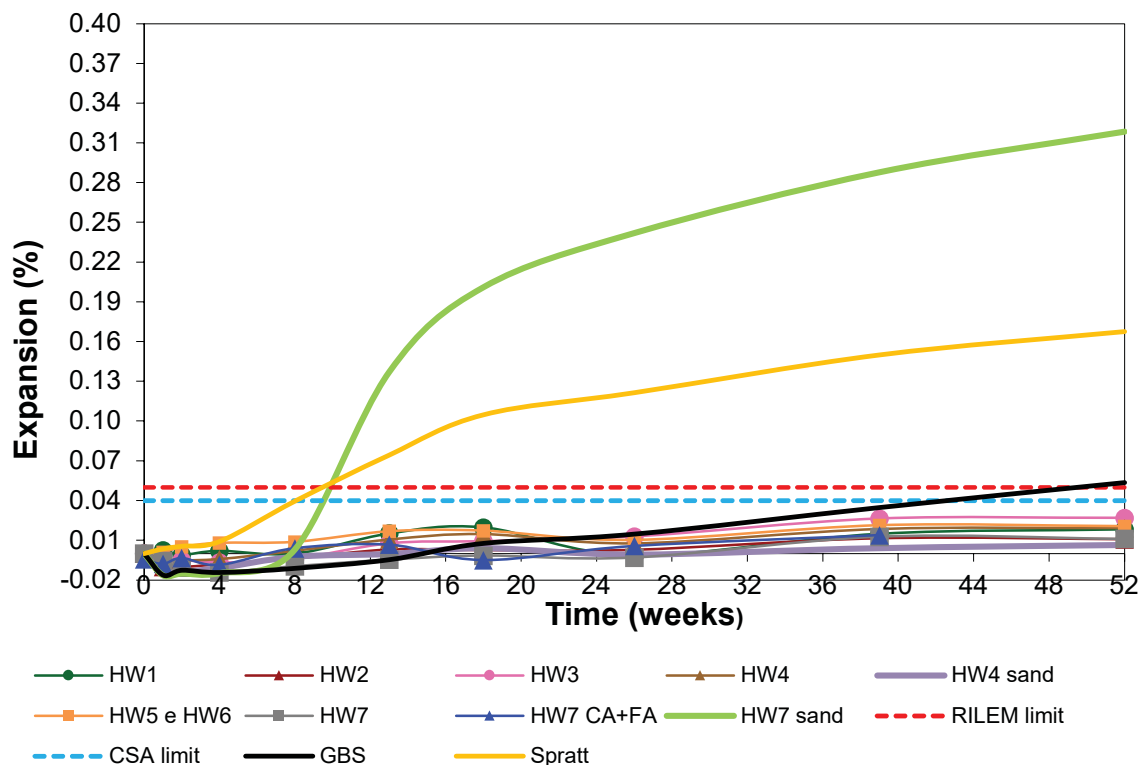


Figure 5.72. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the Canary aggregates.

Iceland

Half of the sets of concrete prisms incorporating Icelandic aggregates show high expansion while the other half does not exceed the expansion limits ($< 0.04\%$ or $< 0.05\%$) (Figure 5.73). At the end of one year of testing, the expansion values of the aggregates with the highest

expansion are: ICL2 fine sand + HP = 0.203%, ICL2 coarse sand + HP = 0.248%, ICL4 = 0.125% and ICL4 sand + HP = 0.341%; the ones with the lowest expansion are: ICL1 = 0.025%, ICL2 = 0.011%, ICL3 sand + HP = 0.01%, ICL3 sand + HP = -0.009%. The expansion took a leap between the 4th/8th and 13th (0.137) week of testing for the prisms with high expansion, starting with negative expansion for some and finishing with high expansion values ranging from 0.125% to 0.341%.

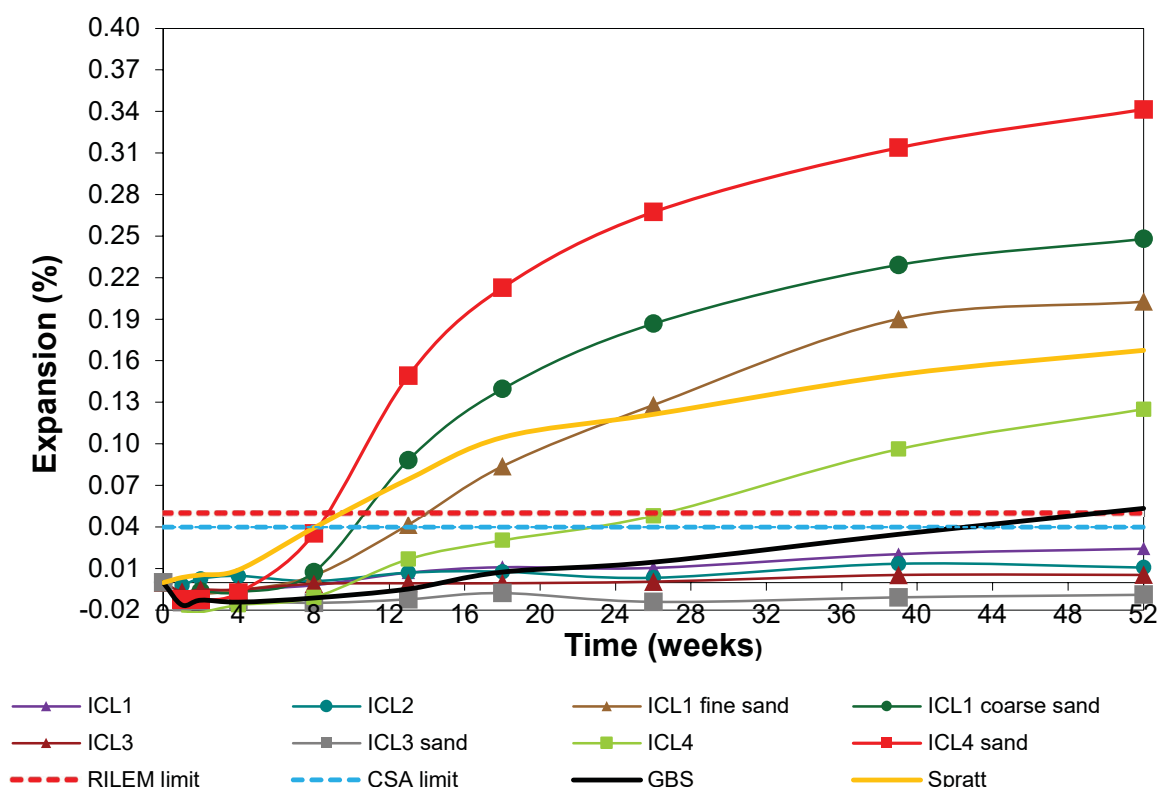


Figure 5.73. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the Icelandic aggregates.

The CPT results showed that half of the Icelandic aggregates tested are considered non-reactive in accordance with the expansion limits indicated in the American and Canadian standards ($< 0.04\%$) and in the RILEM recommendations ($< 0.05\%$). As for the other aggregates, in accordance with the Canadian standard (CSA 23.2-27A, 2019), three are considered highly reactive (ICL1 fine sand + HP, ICL1 coarse sand + HP, ICL4) with expansion values between 0.12% and 0.26% and one is considered very highly reactive (ICL4 sand + HP) with expansion higher than 0.26%. In accordance with the American standard (ASTM C 1778, 2020), two are considered highly reactive (ICL1 fine sand + HP, ICL4) with expansion

values ranging between 0.12% and 0.24% and the other two are considered very highly reactive (ICL1 coarse sand + HP, ICL4 sand + HP) with expansion higher than 0.26%. Also, in accordance with the RILEM recommendations, these four aggregates are considered reactive.

Japan

The CPT for Japan aggregate presents high expansion reaching 0.236% at the end of one year of testing (Figure 5.74). There is some tendency for stabilization with time. Interestingly, after about eight weeks of testing, the expansion curve of the JAP aggregate is somewhat parallel to that of the Spratt control aggregate.

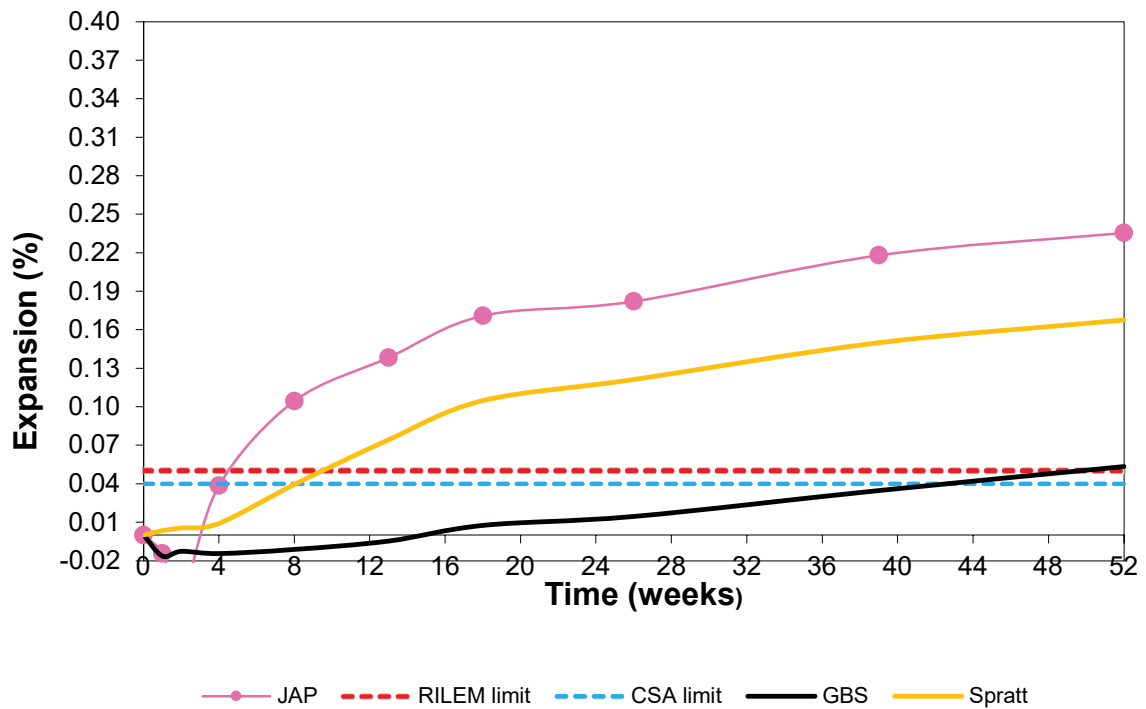


Figure 5.74. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the Japanese aggregates.

According to the limits of expansion indicated in the different standards (CSA 23.2-27A, 2019; ASTM C 1778, 2014) and RILEM recommendations, this aggregate is considered highly reactive for both standards and reactive for RILEM AAR-0 (2016). The results for the CPT method for the Japan aggregate are shown in Figure 5.74.

New Zealand

The concrete prisms made with the New Zealand aggregates show low expansion. At the end of one year of testing, the expansion values are: NZ1 – 0.006%, NZ2 – 0.018% and NZ3 – 0.032%. The expansion started to increase after the 8th week but with a tendency of stabilization was observed in the last weeks.

According to the limits of expansion indicated in ASTM C 1778, (2014) for the American standard and the Canadian standard CSA 23.2-27A (2019) and in the recommendations of RILEM AAR-0 (2016) these aggregates are considered non-reactive.

The results of the CPT method for the New Zealand aggregates are shown in Figure 5.75.

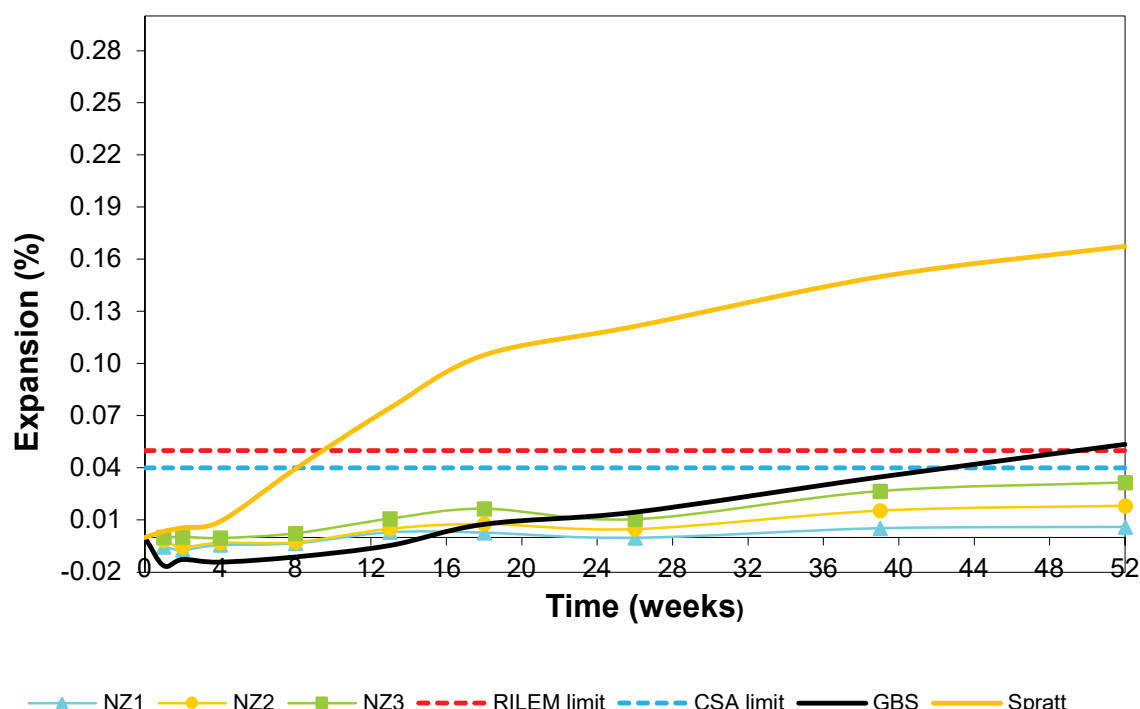


Figure 5.75. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the New Zealand aggregates.

5.1.4.2. Gel Pat Test

The Gel Pat test was performed on all concrete prisms except for the majority of the concretes from the Azores. The test was performed during 19 weeks and photos were taken at 2, 4, 9 and 19 weeks. The quantity of gel produced in each concrete section and at different periods of time allows to classify the ASR intensity into different categories: 0 = no gel, 1 = traces, 2 = some, 3 = fair, 4 = large and 5 = very large.

The results of GPT are presented in Table 5.26.

The results after 19 weeks of testing show that no gel is produced by CRV and NZ1 aggregates. Some gel deposits were found on rare particles of the concrete sections with NZ2 and NZ3 aggregates; however, a white film covering the whole surface developed in the case of the section with NZ3 aggregate. Some deposits and a white film were observed on the sections incorporating the aggregates CANY2, HW2, HW4, HW7 CA + FA, ICL1, ICL2 and ICL4. Several aggregate particles display gel deposits in the samples of HW1, HW5/6 and HW7. In all the sand samples, the gel produced occurs only in the sand fraction (in some or several particles) and no white film is present. JAP and HW3 were the only two concrete sections exhibiting many aggregate particles with gel.

Table 5.26. Results of the GPT after 19 weeks of testing

Samples	GPT (19 w)	Description
CRV	0	No gel
CANY1	2	Gel on some particles; whitish film
CANY2	3.5	
HW1	4	Gel on several particles; whitish film
HW2	3.5	Gel on some particles; $\pm$ whitish film
HW3	3.5	Gel on many particles; whitish film
HW4	3.5	Gel on some particles; whitish film
HW4 sand + HP	1	Gel on several particles of the sand fraction; no whitish film
HW5/6	4	Gel on several particles; whitish film
HW7	3.5	Gel on several particles; $\pm$ whitish film
HW7 CA + FA	3	Gel on some particles; whitish film
HW7 sand + HP	2	Gel on several particles of the sand fraction; no whitish film
ICL1	2.5	Gel on some particles; $\pm$ whitish film
ICL1 Fine sand + HP	3	Gel on several particles of the sand fraction; no whitish film
ICL1 Coarse sand + HP	3	Gel on several particles of the sand fraction; no whitish film
ICL2	3	Gel on some particles; $\pm$ whitish film
ICL3 + HP	3.5	Gel on some particles of GG; $\pm$ whitish film
ICL3 sand + HP	3.5	Gel on some particles of GG; $\pm$ whitish film
ICL4	2.5	Gel on some particles; whitish film
ICL4 sand	2	Gel on several particles of the sand fraction; no whitish film
JAP	5	Gel on many particles; whitish film
NZ1	0	No gel
NZ2	3	Gel on rare particles
NZ3	3.5	Gel on rare particles, whitish film
GG: coarse fraction		

Figures 5.76, 5.77, and 5.78 display different photos of the concrete sections incorporating the various aggregate samples investigated in GPT at week 19. Also, a closer view of some of the samples is presented.

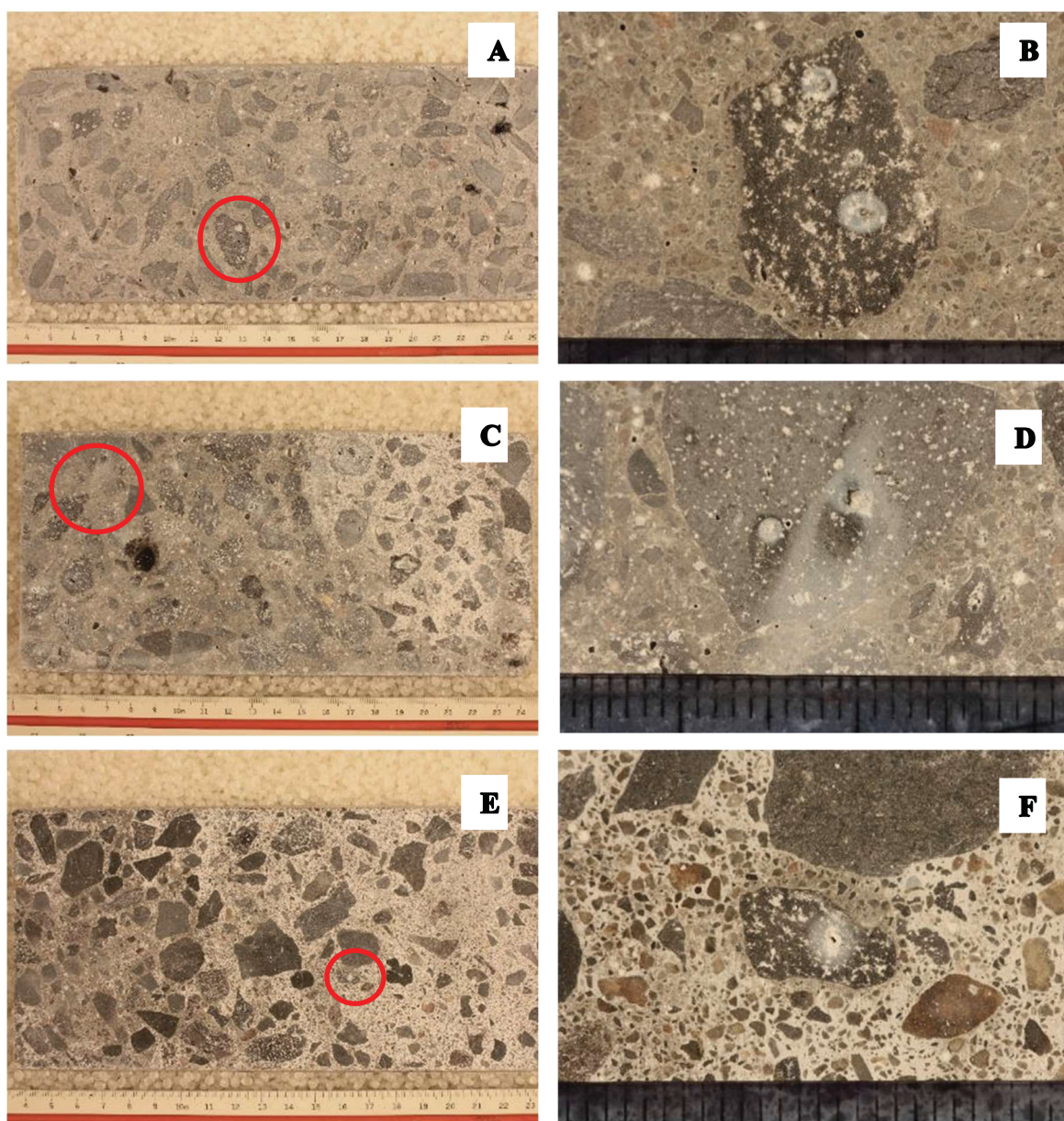


Figure 5.76. Photographs of the results of the GPT were used in different concrete sections at week 19. A) concrete section with CRV aggregate; B) Detail of the concrete (CRV) showing deposits of gel on an aggregate particle; C) Concrete section with CANY2 aggregate; D) Detail of the concrete (CANY2); E) Concrete section with CANY1 aggregate; F) Detail of the concrete (CANY1) with one deposit of gel on an aggregate particle.

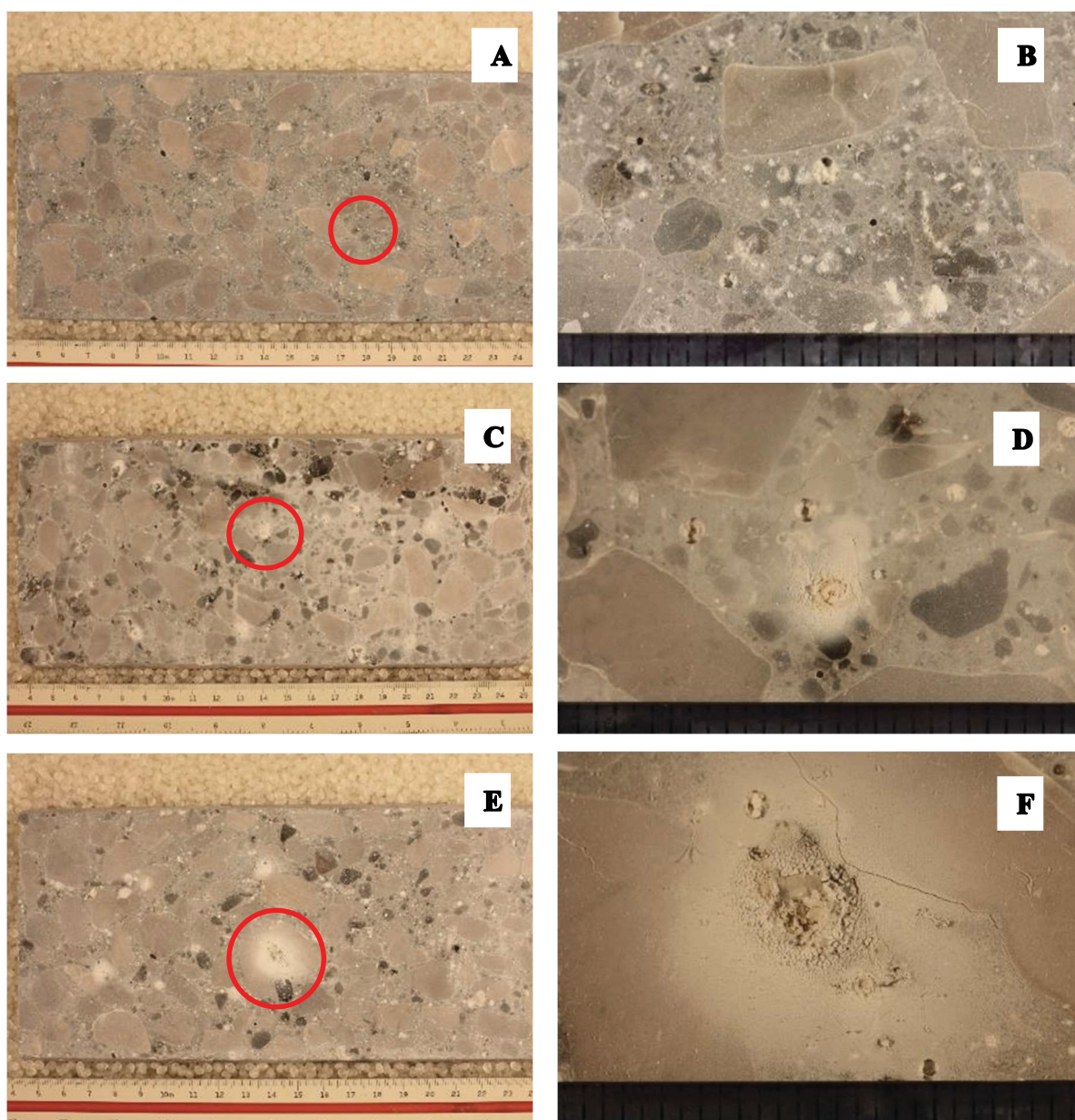


Figure 5.77. Photographs of the results of the GPT were used in different concrete sections at week 19. A) Concrete section with HW7 sand aggregate; B) Detail of the concrete section (HW7 sand) showing deposits of gel on sand particles; C) Concrete section with ICL1 coarse sand aggregate; D) Detail of the concrete section (ICL1 coarse sand) showing deposits of gel on sand particles; E) Concrete section with ICL1 fine sand aggregate and F) Detail of the concrete section (ICL1 fine sand) showing deposits of gel on sand particle and white film of gel covering the section.

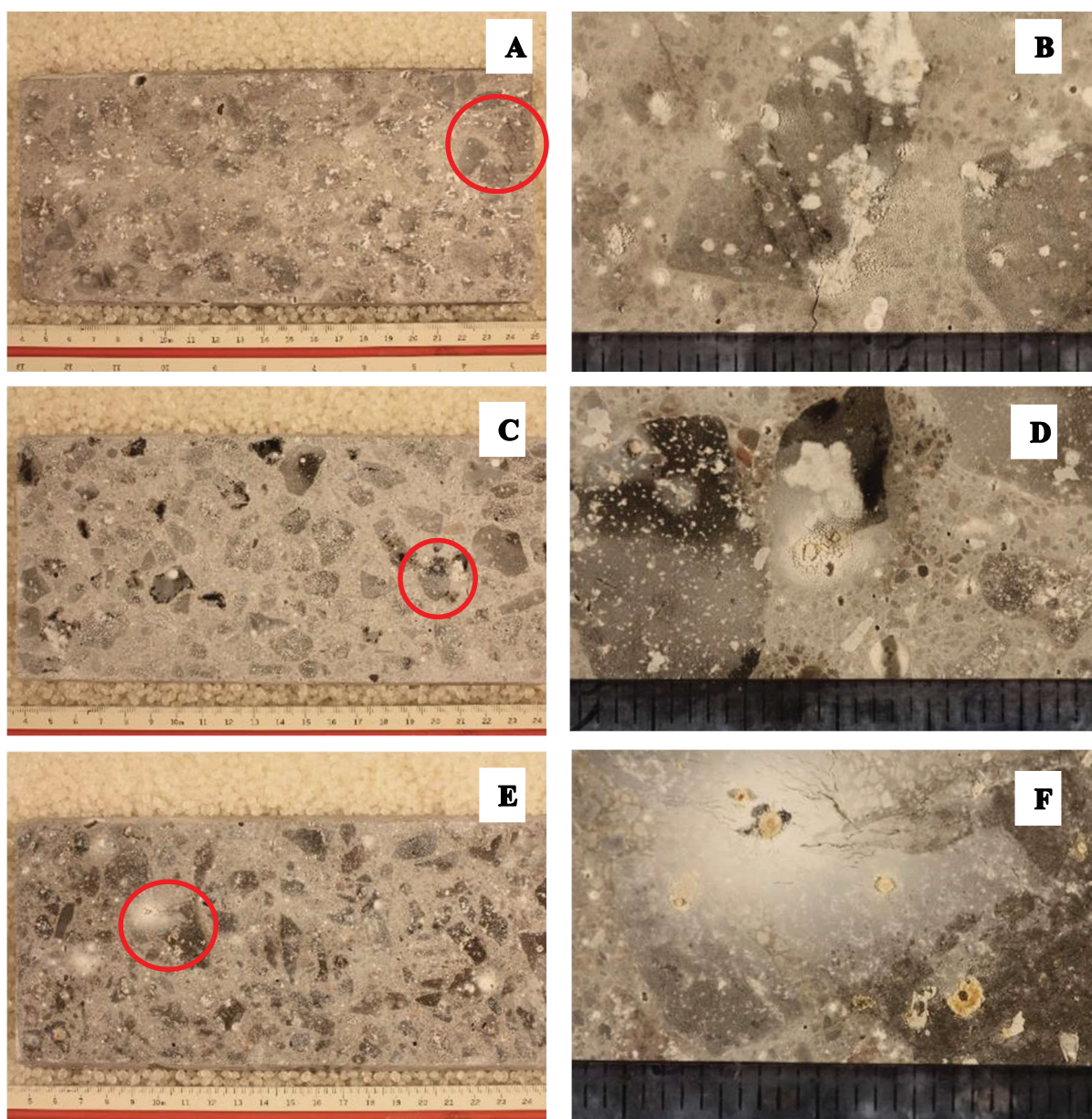


Figure 5.78. Photographs of the results of the GPT were used in different concrete sections at week 19. A) Concrete section with JAP aggregate; B) Detail of the concrete section (JAP) showing numerous deposits of gel on coarse aggregate particles; C) Concrete section with NZ2 aggregate; D) Detail of the concrete section (NZ2) showing deposits of gel on some coarse aggregate particles; E) Concrete section with NZ3 aggregate; F) Detailed of the concrete section (NZ3) showing deposits of gel and white film of gel at the surface of the section.

5.1.4.3. Petrographic examination - Damage Rating Index (DRI)

The DRI was performed for the majority of the concrete prisms. The results are shown in Tables 5.27 and 5.28.

Table 5.27. Detailed results of the number of counts multiplied by the weighting factor of reaction features for each concrete prism sample at the end of one year of testing ((Villeneuve et al., 2012).

Samples	CCA	OCA	CA+RP	Deb	RAP	CCP	CCP+RP	DRI
SMA-SM1	27	127	8	9	4	46	16	238
SMA-SM2	13	85	0	54	0	59	0	210
SMG-SM1	21	76	0	5	0	9	2	114
SMG-SM2	25	44	2	2	0	11	2	86
SMG-SM3	8	26	10	16	0	11	4	74
TER-SM1	17	60	12	26	0	67	20	203
TER-SM2	33	86	0	11	0	89	0	219
GRA-SM1	9	169	4	2	0	47	6	235
SJO-SM1	9	13	0	9	0	18	0	49
PIC-SM1	22	56	0	2	0	13	2	94
FAI-SM1	25	40	0	4	0	80	0	149
FLO-SM1	27	26	1	185	0	797	1	1039
FLO-SM2	11	110	0	11	0	105	4	240
CANY2	34	173	1	0	2	7	9	225
HW3	18	142	11	1	0	3	3	178
HW4	20	38	1	0	0	0	0	59
HW5/6	14	65	21	1	1	11	0	114
HW7	12	77	13	1	0	9	0	112
HW7CA+FA	43	129	1	0	0	21	0	194
HW7 sand	93	418	467	3	3	99	2291	3373
ICL1	11	164	36	13	13	89	63	388
ICL1 F sand	165	350	130	31	22	151	569	1417
ICL1 C sand	157	203	249	36	27	267	939	1877
ICL4	28	269	32	30	5	210	47	620
ICL4 sand	62	760	120	64	10	450	659	2125
JAP	24	515	85	4	1	296	283	1208
NZ2	15	4	0	0	0	3	0	21
NZ3	10	36	6	1	0	9	6	67
Spratt	67	761	215	17	9	28	172	1270
GBS	151	166	34	9	6	69	30	449

The DRI method showed that the majority of the concrete prisms from the Azores do not have that many cracks in the cement matrix or in the aggregate particles and have minor reaction products in the air voids. Overall, the concrete prisms are in good condition. Based

on Table 5.27, the only concrete that shows a high number of cracks in the cement matrix and within the aggregates is the FLO-SM1 aggregate. However, no gel is found in the cracks. Figures 5.79A and B show the photomicrographs obtained from: A) the concrete with FAI-SM1 aggregate where one crack is visible in an aggregate particle; and B) the concrete with FLO-SM1 aggregate where open cracks in the cement paste and a partial debonding of the aggregate particle are visible.

Table 5.28. Concrete condition and degree of deterioration based on the DRI results (Villeneuve, 2011; Villeneuve et al., 2012; Fournier et al., 2015).

Samples	DRI	Degree of deterioration
SMA-SM1	238	Trace – Concrete in good condition
SMA-SM2	210	Trace – Concrete in good condition
SMG-SM1	114	Trace – Concrete in good condition
SMG-SM2	86	Trace – Concrete in good condition
SMG-SM3	74	Trace – Concrete in good condition
TER-SM1	203	Trace – Concrete in good condition
TER-SM2	219	Trace – Concrete in good condition
GRA-SM1	235	Trace – Concrete in good condition
SJO-SM1	49	Trace – Concrete in good condition
PIC-SM1	94	Trace – Concrete in good condition
FAI-SM1	149	Trace – Concrete in good condition
FLO-SM1	1039	Severe to very severe - Concrete with severe signs of deterioration
FLO-SM2	240	Trace – Concrete in good condition
CANY2	225	Trace – Concrete in good condition
HW3	178	Trace – Concrete in good condition
HW4	59	Trace – Concrete in good condition
HW5/6	114	Trace – Concrete in good condition
HW7	112	Trace – Concrete in good condition
HW7CA+FA	194	Trace – Concrete in good condition
HW7 sand	3373	Very severe - Concrete with severe signs of deterioration
ICL1	388	Fair to moderate – Concrete generally in good condition
ICL1 F sand	1417	Severe to very severe - Concrete with severe signs of deterioration
ICL1 C sand	1877	Severe to very severe - Concrete with severe signs of deterioration
ICL4	620	Moderate to severe - Concrete with moderate signs of deterioration
ICL4 sand	2125	Very severe - Concrete with severe signs of deterioration
JAP	1208	Severe to very severe - Concrete with severe signs of deterioration
NZ2	21	Trace – Concrete in good condition
NZ3	67	Trace – Concrete in good condition
Spratt	1270	Severe to very severe - Concrete with severe signs of deterioration
GBS	449	Moderate to severe - Concrete with moderate signs of deterioration

The same is verified for the concrete prism with New Zealand aggregate. Cracks are rare in the cement matrix or within the aggregate particles (Figure 5.80A); rare gel is observed, only in a few air voids and rarely appears in some cracks, as is shown in Figure 5.80B. Table 5.29 shows that NZ3 is the one with more cracks but still both concretes present good conditions.

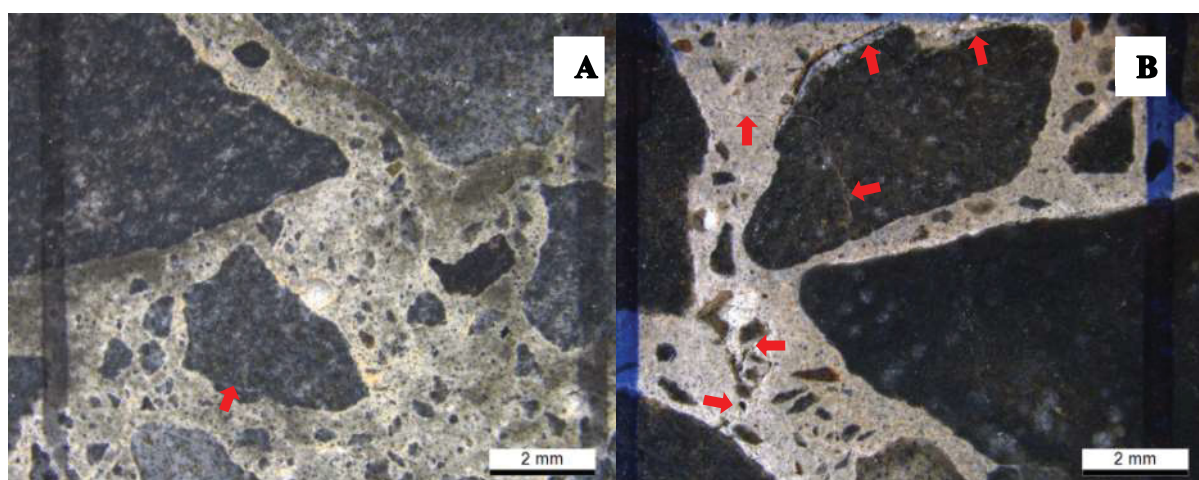


Figure 5.79. Photographs were obtained under a stereo binocular microscope of Azorean concrete prisms. A) Concrete with no cracks in the cement paste and only showing a closed crack in the aggregate particle in the centre of the image (FAI-SM1); B) Concrete with open cracks in the cement paste, closed crack in the aggregate particle and partially debonding of the aggregate particle in the upper part of the image (FLO-SM1).

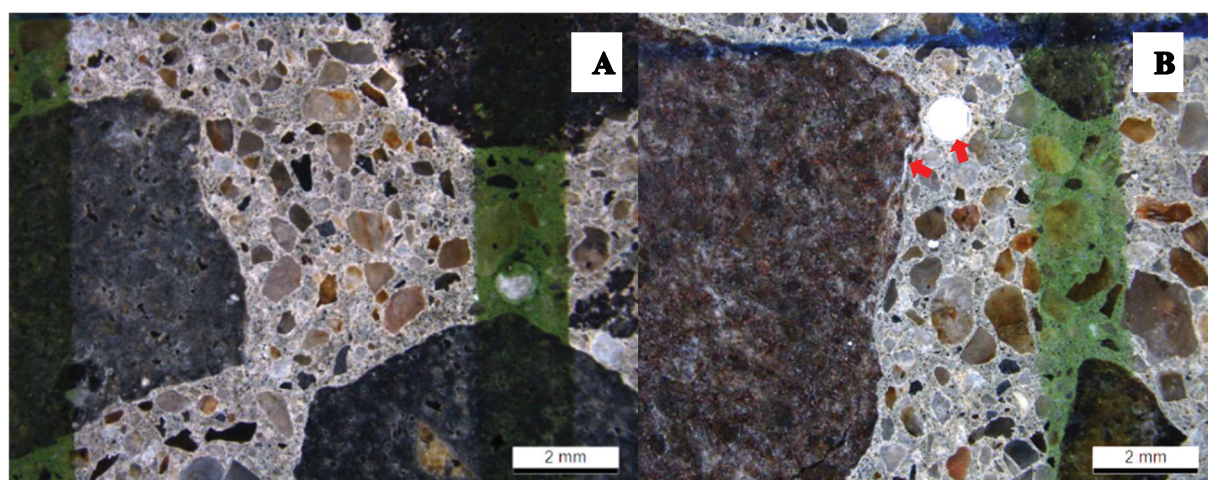


Figure 5.80. Photographs of concrete prisms incorporating New Zealand aggregates. A) Concrete with no cracks in the cement paste and in the aggregate particles (NZ2); B) Concrete with open cracks in an aggregate particle and an air void filled with ASR gel (NZ3).

The Hawaiian concrete slabs show minor cracks, mainly closed cracks in the aggregate particles, and some (few) cracks in the cement paste. The only exception is HW7 sand + HP, which shows high a quantity of cracks with ASR gel crossing or lining the particles of the sand fraction and in the cement matrix. It is observed that the ASR gel is originated from the volcanic fine aggregate particles and not from the HP coarse aggregate. In the case of the HP aggregate, the gel sometimes surrounds the particles and in other cases, it even crosses them. Cracks occur connecting reactive aggregate particles. Figure 5.81 (A, B, C and D) shows some features of the HW7 sand.

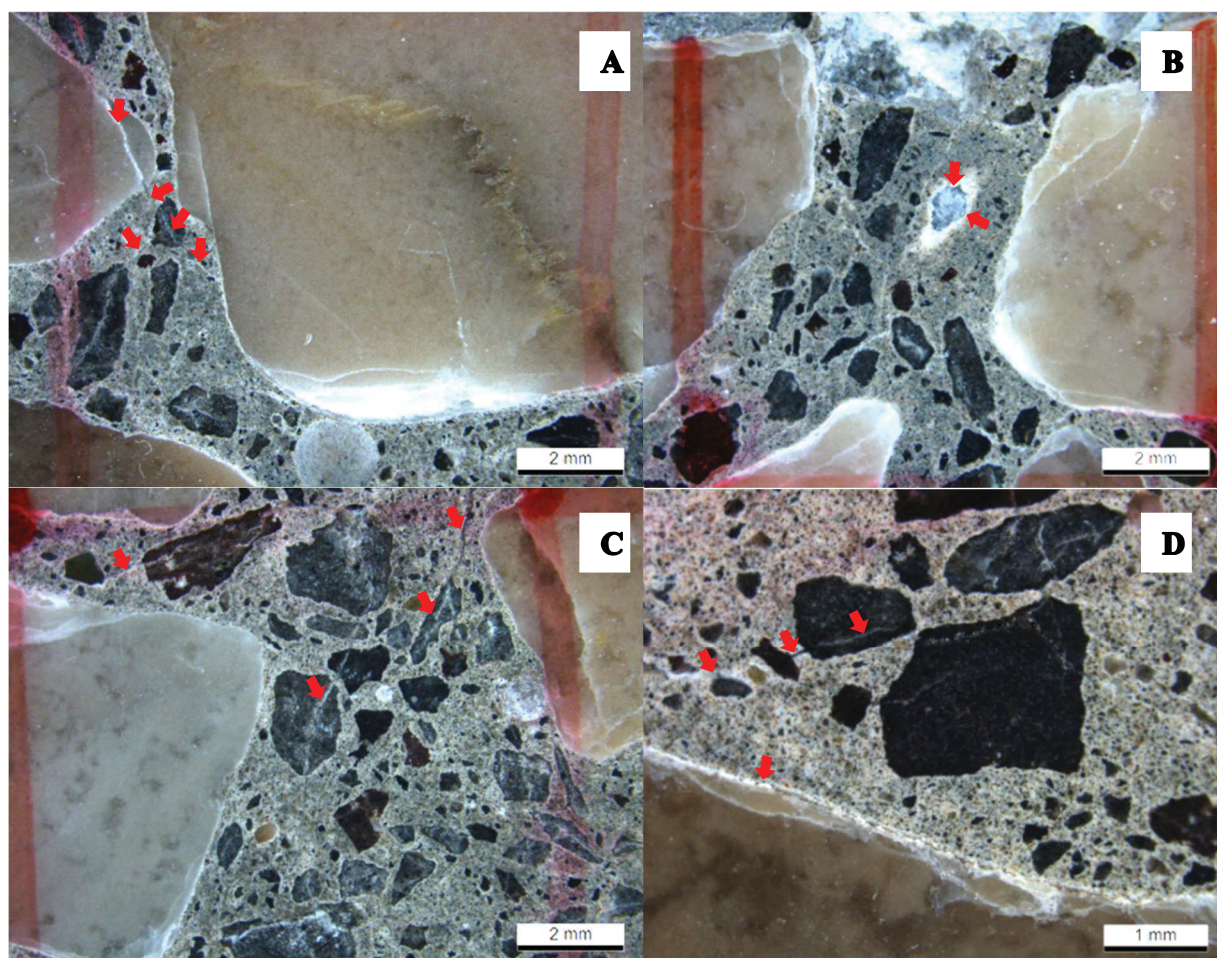


Figure 5.81. Photographs of concrete prism incorporating HW7 sand and HP (non-reactive) coarse aggregate. A) Concrete with several cracks in the cement matrix and crossing different basalt aggregate particles and HP particles, as pointed by the red arrows; B) Concrete with a reacted aggregate particle (red arrows); C) Several cracks in the basalt particles and also in the cement matrix, with gel (red arrows); D) Gel lining an HP particle and a basalt particle with gel, extending into the cement paste and crossing and lining other particles.

The Icelandic concrete prisms present a high quantity of cracks in the aggregate particles and in the cement matrix, more frequent in the concretes containing the Icelandic sand fraction. Also, these prisms contain much more reaction products either in the cracks within the

aggregate particles or in the cracks of the cement paste. Figure 5.82 (A, B, C and D) shows some features of the Icelandic polished sections with reactive sands.

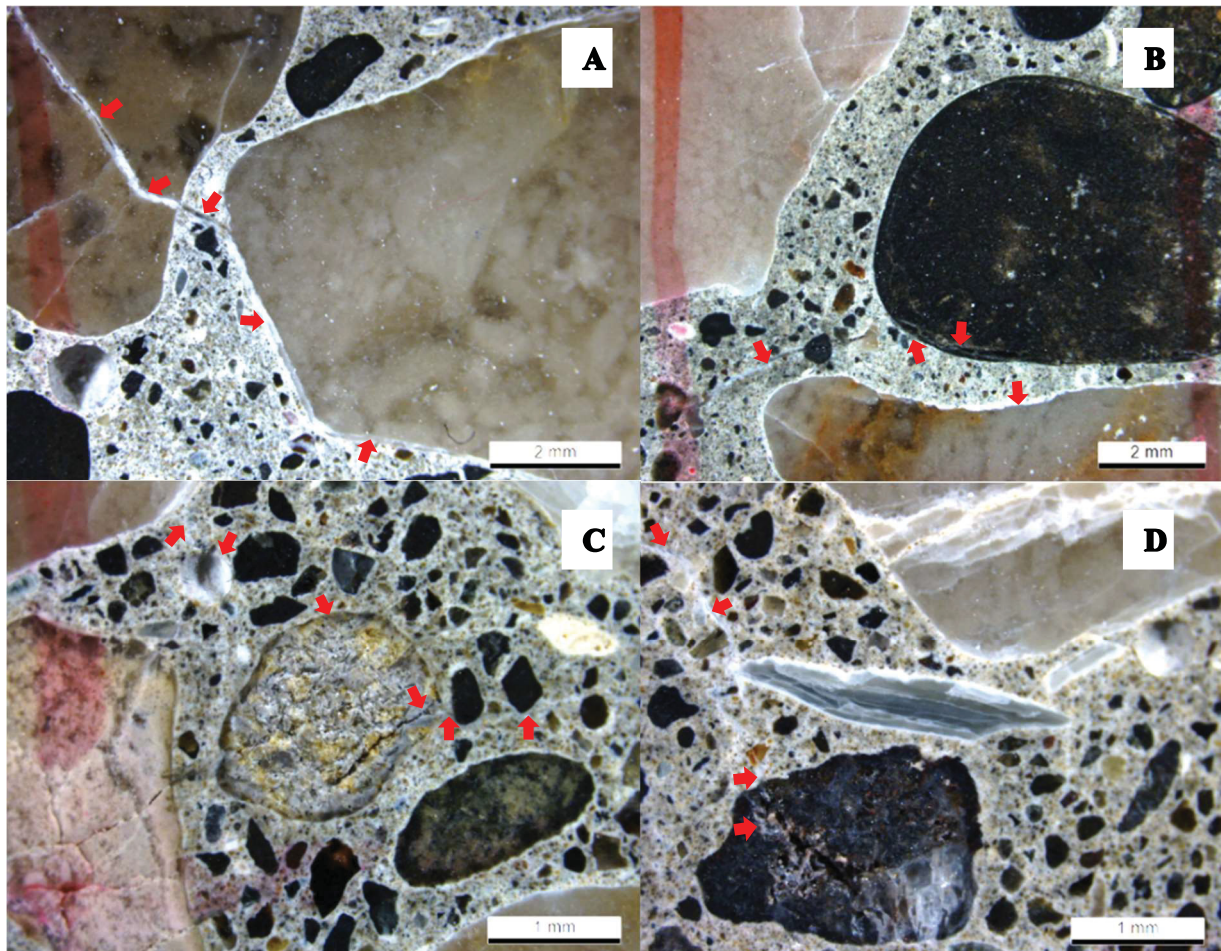


Figure 5.82. Photographs of concrete prisms incorporating ICL1 coarse and fine sands. A) Concrete with a crack with gel crossing HP particle and lining other HP particle (ICL1 coarse sand); B) Basalt with an open crack partly filled with reaction product, that extends into the cement paste and an HP particle rimmed by gel (red arrows); C) Reactive particle with ASR gel extending into the cement matrix and pore partly filled with gel (ICL1 fine sand) (red arrows); D) Basalt particle with an open crack and gel partially filling cracks in the cement paste (ICL1 fine sand).

The concrete with JAP aggregate displays several cracks in a large proportion of the aggregate particles, with some of them being filled with ASR gel. The cracks extend into the cement paste with some of them being filled with gel. Figure 5.83A and B show some of the features found in the concrete slab.

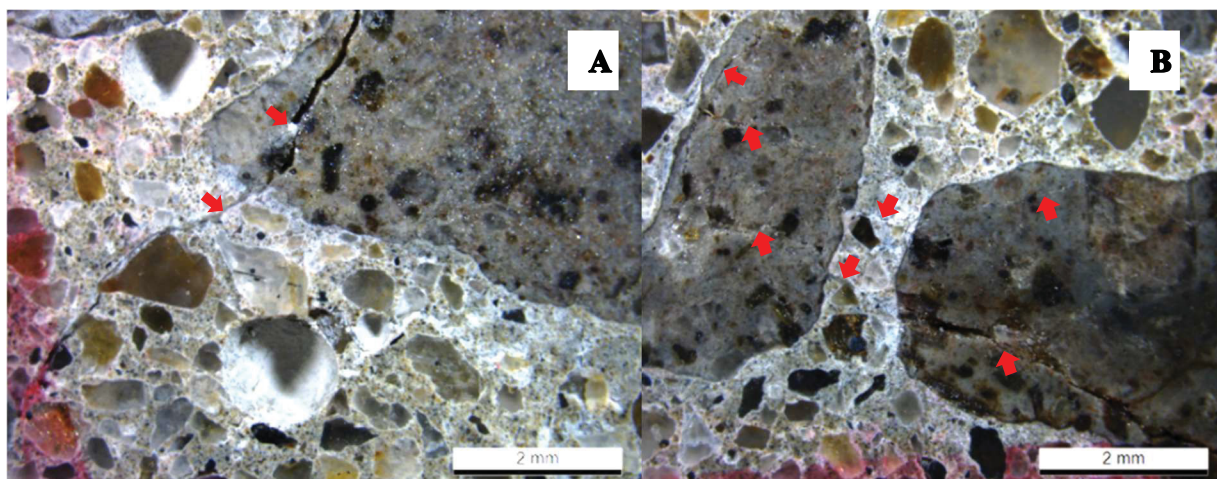


Figure 5.83. Photographs of concrete prisms incorporating the JAP aggregate. A) Open crack with some gel in an andesite aggregate particle extending into the cement paste; B) Several open cracks in the two andesitic aggregate particles and gel in the cement paste (red arrows).

5.1.4.4. Post-mortem concrete petrography

All the concrete aggregates are crushed rocks, except for three gravel aggregates from Iceland (ICL1, ICL2 and ICL4); in accordance with the CPT method used in this study, they were all tested with equal quantities of the following particle sizes: 20 to 14, 14 to 10 and 10 to 5 mm. The (non-reactive) sand used at Université Laval is the same for all mixtures aiming at evaluating the potential alkali reactivity of coarse aggregates, including CRV aggregate (Azores), and consists of natural sand with feldspars (alkali feldspar and plagioclase), quartz, clinopyroxene (aegirine-augite), opaque minerals and biotite. However, there are some cases where HP is used as the coarse aggregate to evaluate the reactivity of volcanic sands, which are: HW4 sand, HW7 sand, ICL1coarse sand, ICL1fine sand and ICL4 sand. For the concrete prisms incorporating the Azorean aggregates, the fine aggregate used has the same composition as the coarse aggregates.

For all concrete prisms, the cement paste is homogeneous.

Azores Archipelago (Portugal)

The aggregates in the Azorean concrete prisms are composed of basanites (SMA-SM1, SMA-SM2), basalts (SMG-SM3, TER-SM2, SJO-SM1, PIC-SM1), hawaiites (SMG-SM1, SMG-SM2, GRA-SM1, FAI-SM1), potassic trachybasalts (SMG-SM1, SMG-SM2), mugearite (FLO-SM1), benmoreite (FLO-SM2) and trachyte (TER-SM1). In general, the more basic aggregate particles have intergranular textures with olivine, clinopyroxene and plagioclase. Intersertal texture is only observed in the concrete with FLO-SM2 aggregate where an amount

of volcanic glass was observed, and some sections also contain a mix of chlorite and smectite. In some aggregate particles, the olivine crystals are rimmed by iddingsite. The groundmass is composed of plagioclase, clinopyroxene, opaque minerals and rare volcanic glass. Trachyte is composed of alkali feldspar, clinopyroxene, amphibole, opaque minerals and biotite.

Some aggregate particles show a very dark tachylite groundmass or an orange to brown colour in the rock groundmass, probably an indication that the rock is more oxidized. Also, some glassy basalt particles are present in some of the concrete prisms.

In general, there are few to some cracks in the cement matrix and most of the aggregate particles are not cracked. However, aggregate particles are debonded in different concrete samples (SMG-SM2). The air voids are usually empty.

There are two exceptions related to the concrete prisms made with SMA-SM1 and SMA-SM2 aggregates. They both display several cracks inside the aggregate particles, some of them being filled with an isotropic yellow material (Figure 5.84A); also, it seems that iddingsite is sometimes part of the material filling the cracks. In these two concrete samples, there are more cracks in the aggregate particles than in the cement matrix. Also, some debonding of the aggregate particles from the cement matrix is noticed. In the concrete samples, some isotropic beige gel is visible in SMA-SM1 (Figure 5.84B and C) and glass inside an aggregate particle in SMA-SM2 (Figure 5.84D). The air voids are usually empty. In concrete with SMA-SM2 aggregate, the limit between the aggregate particles and the cement matrix is difficult to define due to the very dark colour of the rock.

In all concrete samples, there is no evidence of an ongoing ASR; therefore, there is no visible damage. However, concrete incorporating SMA-SM1 and SMA-SM2 shows that the aggregate particles are cracked and they both contain gel; on the other hand, the cement matrix is not cracked and the gel is restricted to the aggregate particles.

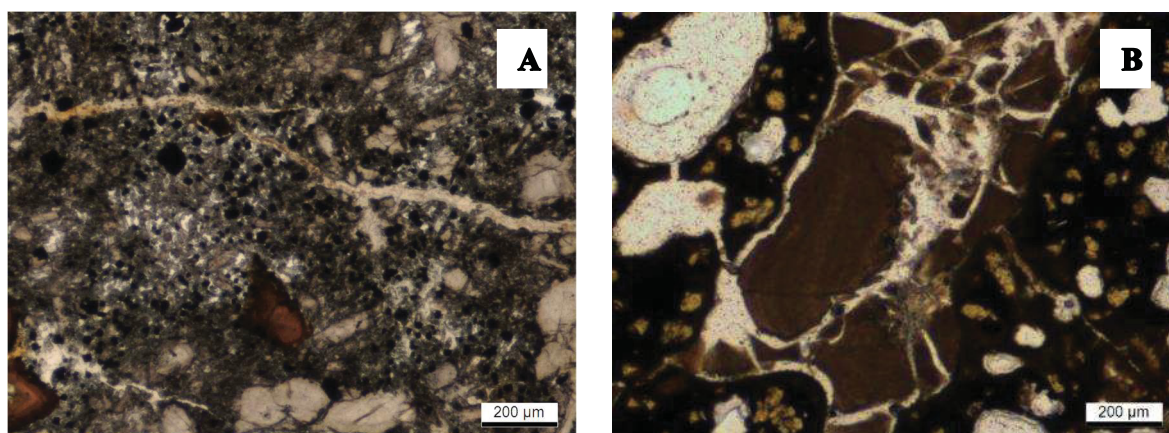


Figure 5.84. Photomicrographs of concrete prisms incorporating Azorean aggregates. All photos are in PPL. A) Crack inside an aggregate particle with a yellowish material (SMA-SM2); B) Gel inside an aggregate particle associated with volcanic glass (SMA-SM1).

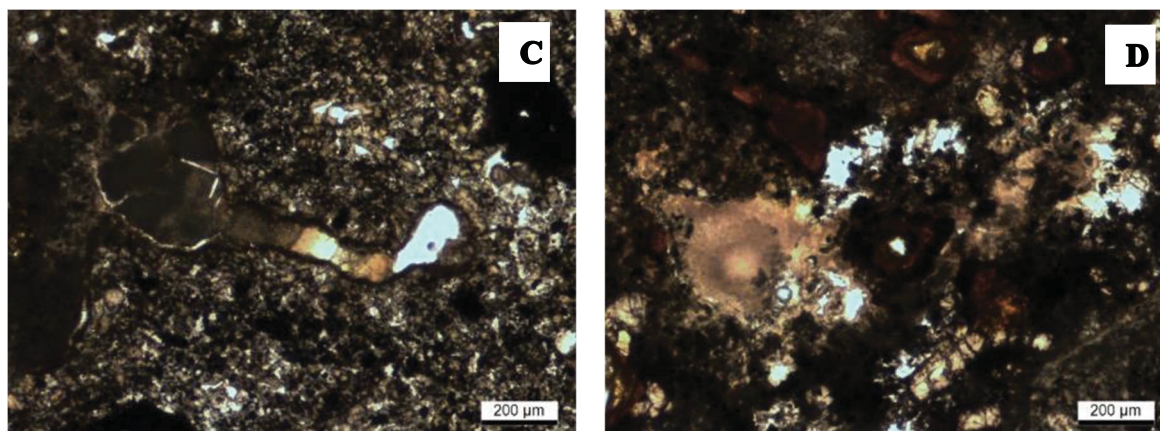


Figure 5.84. (continued). Photomicrographs of concrete prisms incorporating Azorean aggregates. All photos are in PPL. C) Gel inside an aggregate particle (SMA-SM1); D) Glass inside an aggregate particle (SMA-SM2).

Canary Islands (Spain)

The concrete thin sections show that the aggregates correspond to basanite. In general, the aggregate particles contain phenocrysts of olivine (some with 0.6 mm width) and clinopyroxene and minor plagioclase set in an intersertal and intergranular groundmass. In some aggregate particles, the olivine crystals are rimmed or completely altered to iddingsite and sometimes show peculiar textures. The opaque minerals are present either in the phenocrystalline phase or in the matrix. The groundmass contains plagioclase, clinopyroxene, opaque minerals and brownish volcanic glass. The presence of zeolites was identified in one aggregate particle with a radial habit filling the vesicles of the rock (Figure 5.85A). Some aggregate particles contain a very dark tachylite groundmass.

In general, there are some small cracks in the cement matrix that connect the aggregate particles with some grains of the sand fraction (Figure 5.85B) or to air voids. There are only very few cracks in the aggregate particles (Figure 5.85C) and in both locations the cracks are empty. The majority of the air voids are empty and the others are lined with an isotropic brownish material (Figure 5.85D).

In this concrete there is no evidence of an ongoing ASR, therefore there is no visible damage.

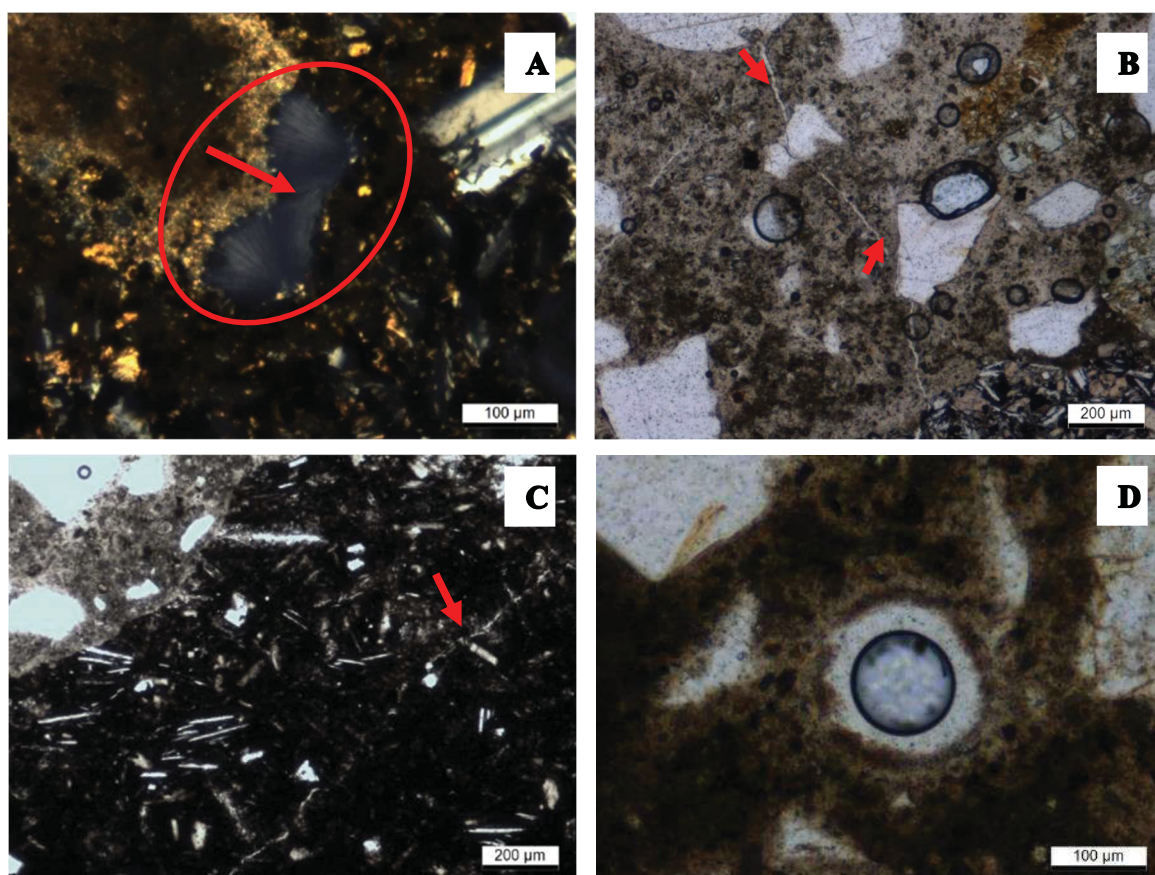


Figure 5.85. Photomicrographs of concrete prisms incorporating Canary aggregate (CANY2). All photos are in PPL. A) Zeolites in a vesicle of an aggregate particle; B) Crack connecting different grains of the sand fraction; C) Crack inside an aggregate particle; D) Air void lined by brownish material.

Hawaiian Islands (USA)

The Hawaiian concrete thin sections show that the aggregates are composed of basaltic rocks, one of them being a mugearite (HW4). In general, the aggregate particles have intergranular and intersertal textures, some of them with phenocrysts of olivine (HW1, HW4, HW5/6, HW7) or/and plagioclase (HW7) or/and clinopyroxene (HW7). Subophitic and variolitic textures are also present in some of the aggregate particles (HW2). The groundmass contains plagioclase, clinopyroxene, opaque minerals and brownish volcanic glass either in the interstices or in vesicles. Some aggregate particles have a black tachylite groundmass.

In general, there are some cracks in the cement matrix (Figure 5.86A) and also inside the aggregate particles (Figure 5.86B). However, in some concrete samples, the aggregates do not have cracks (HW2, HW7) and there are only very few cracks in the cement matrix (HW2). In both cases, the cracks are empty. The majority of the air voids are empty. The other air

voids are lined with an isotropic brownish material (Figure 5.86C) (HW1, HW2, HW3), or filled with the same material (HW7).

In the concrete with HW7 coarse and fine aggregate, the sand fraction is composed of the same rock as the coarse aggregate. Some cracks are filled with a dark brownish material (Figure 5.86D), and in one case, the gel also surrounds the aggregate particle (Figure 5.86E). It is important to mention that none of the aggregate particles are cracked.

In the concrete made with HW7 sand + HP, a few basaltic sand particles are cracked as well as the (non-reactive) limestone aggregate particles. The cement matrix has several cracks (Figure 5.86F).

The majority of the Hawaiian concretes do not show evidence for an ongoing ASR.

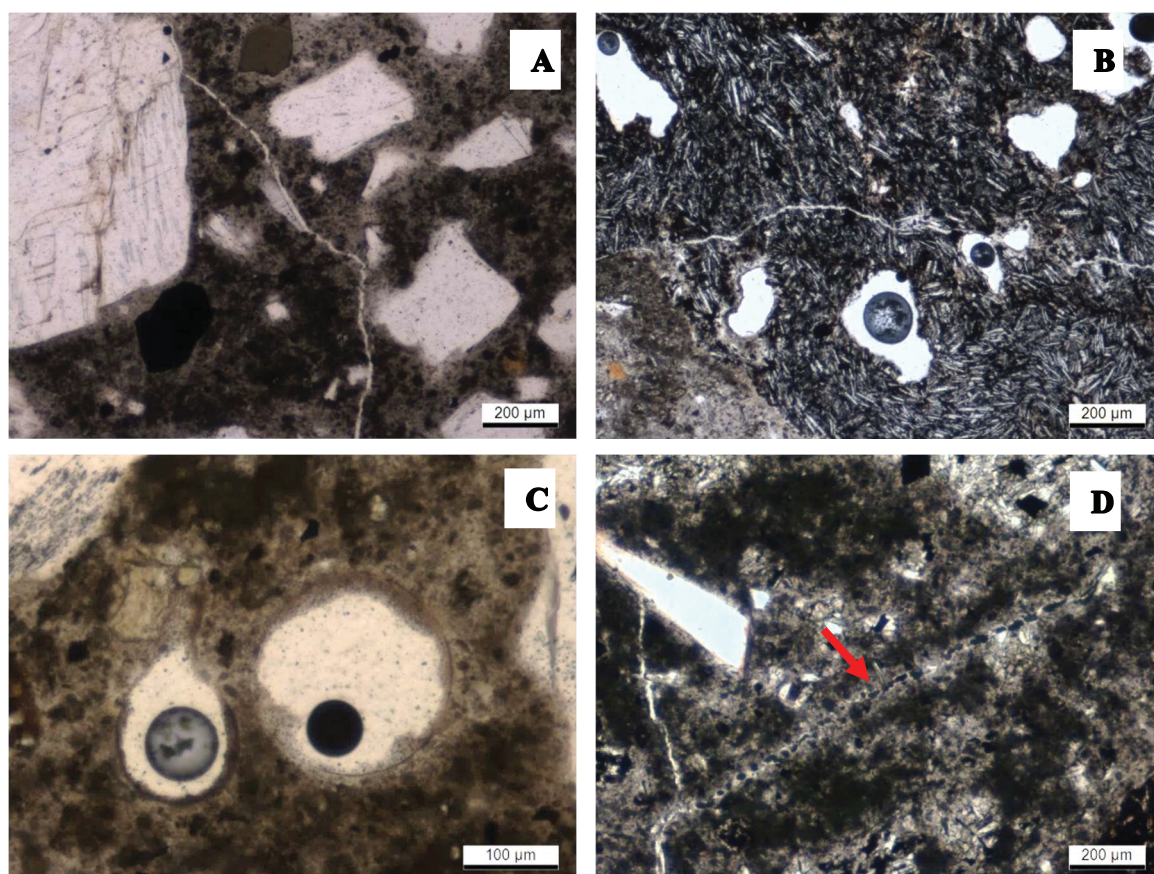


Figure 5.86. Photomicrographs of concrete prisms incorporating Hawaiian aggregates. All photos are in PPL. A) Crack in the cement matrix (HW1); B) Crack inside an aggregate particle (HW4); C) Two air voids lined by brownish material (HW3); D) Crack crossing the cement paste (HW7 CA+FA).

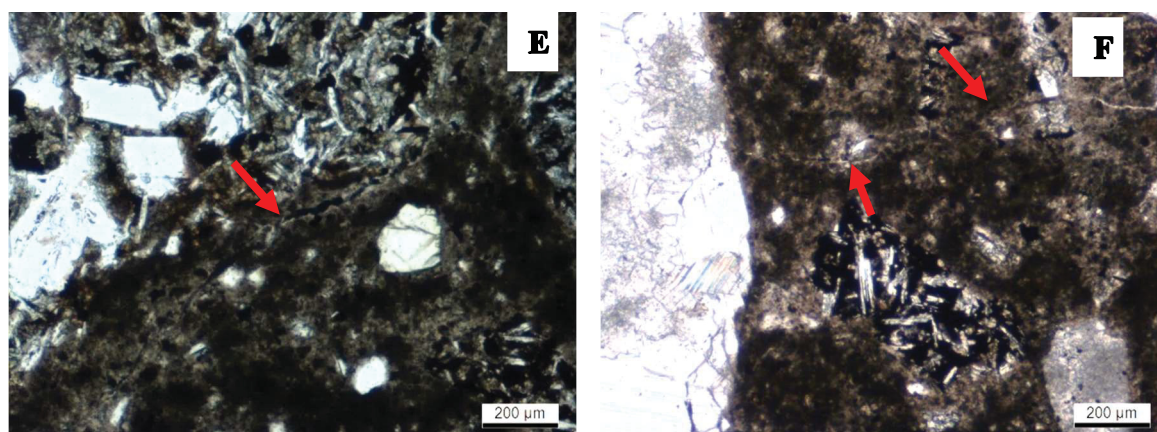


Figure 5.86. (continued). Photomicrographs of concrete prisms incorporating Hawaiian aggregates.

All photos are in PPL. E) Crack in the cement paste and surrounding the aggregate particle (HW7 CA+FA); F) Crack in the cement paste (HW7 sand).

Iceland

The Icelandic concretes thin sections show that the majority of the aggregates are gravels that are composed mainly of basalt with different degrees of alteration, as well as rhyolites. Only one concrete has crushed basalt rocks (ICL3).

The basalt aggregate particles from the gravels have intergranular and intersertal textures, with plagioclase, olivine, clinopyroxene, opaque minerals and fresh and altered volcanic glass; some contain amygdaloids of celadonite and a mix of smectite and chlorite. There are also basalt particles with dark tachylite groundmass and glassy basalt aggregate with crystals mainly of plagioclase. Subophitic and variolitic textures are also present in some of the aggregate particles. Rhyolite is almost aphyric with the presence of a minor quantity of phenocrysts of plagioclase and sanidine. Grains of quartz are visible and devitrified glass forms the darker areas of the rock.

In the concrete with ICL1 aggregate, the cement matrix has some cracks while the presence of cracks in the aggregates is rare. One crack is observed in one sand particle; however, no gel was found. In the concrete with ICL1 coarse sand + HP, the cement matrix has several cracks, some partly filled with a dark brownish material. On the other hand, the majority of the aggregate particles are not cracked, except for some in the sand fraction. Some of these cracks are found in some glassy basalt particles (Figure 5.87A), in a particle that is altered into chlorite and smectite and also in a rhyolite particle (Figure 5.87B), the last one with brownish material. It is noticed that some of the aggregate particles are outlined by brownish material (Figure 5.87C); this includes either the limestone or the basalt particles but is more common in HP aggregate. The air voids are lined or partly filled with brownish material. In the concrete with

ICL1 fine sand + HP, the cement matrix has several cracks, some of them being very large but most are empty (Figure 5.87D). It is observed that besides the cracks in the particles of smaller size, some of the larger aggregate particles are cracked, especially the limestone particles (Figure 5.87E); this is something that did not happen with significant frequency to the concrete with ICL1 coarse sand + HP.

In concrete with ICL2 aggregate, there are some cracks present in the cement matrix and very few in the aggregate particles, only observed in the glassy basalt particles (Figure 5.87F). In both locations, there is no gel present, only some air voids are lined with a brownish material. The same brownish material is rarely present in the cracks and in the air voids is rare.

In concrete with ICL3 aggregate, there are some cracks present in the cement matrix that are connecting only the grains of the sand fraction; however, they seem to be closed cracks (Figure 5.87G).

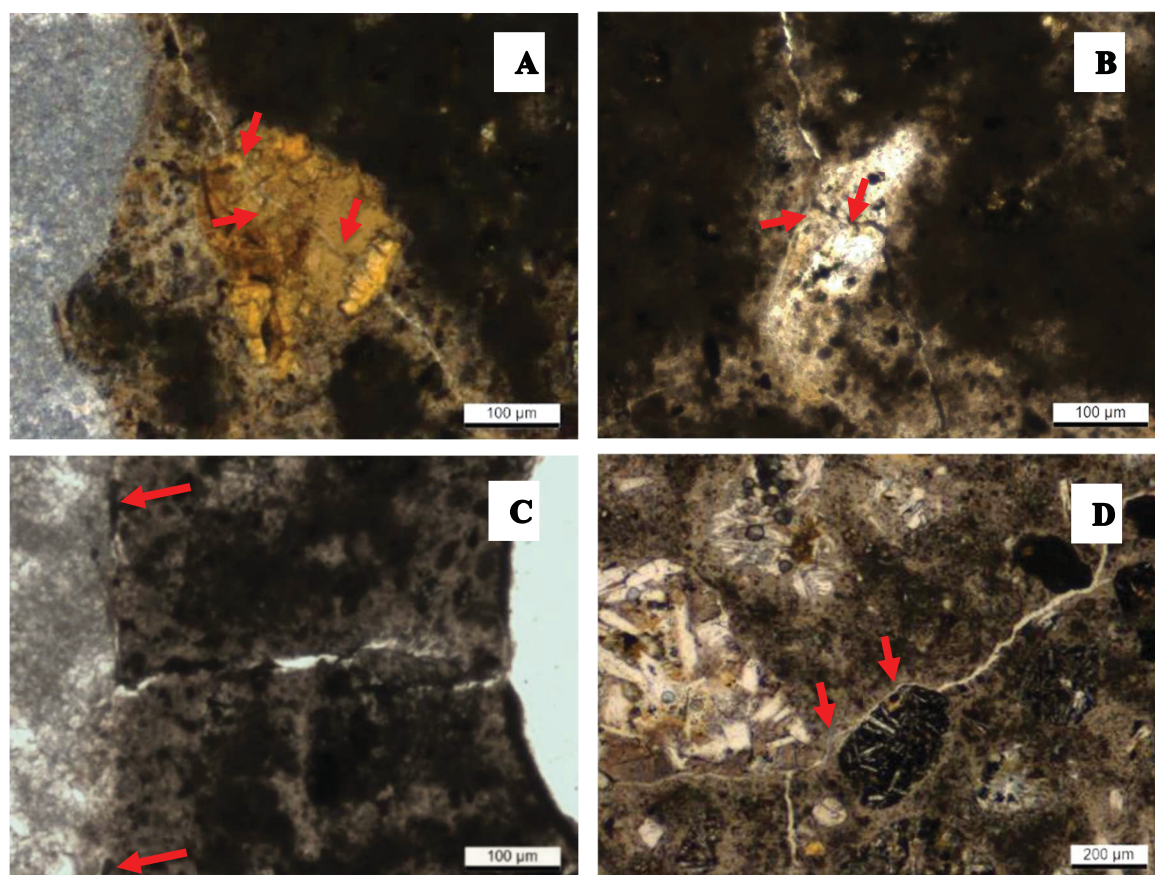


Figure 5.87. Photomicrographs of concrete prisms incorporating Icelandic aggregates. All photos are in PPL. A) Crack crossing glassy basalt particle (ICL1 coarse sand); B) Crack crossing a rhyolite particle and the cement paste (ICL1 coarse sand); C) Limestone aggregate particles outlined by brownish material and connecting by a crack with an air void (ICL1 coarse sand); D) Crack in the cement matrix outlining some aggregate particles (ICL1 fine sand).

There are no cracks in the aggregate particles. In ICL3 sand + HP, some cracks occur in the cement matrix and only a few cracks in the aggregate particles of the sand fraction and in one of the limestone particles are visible. The presence of brownish material in the cracks and in the air voids is rare.

In concrete with ICL4 aggregate, there are few cracks present in the cement matrix. There is a rhyolite aggregate particle with some cracks and a small part of the particle is partly outlined with a brownish material (Figure 5.87H). Most pores are empty. In ICL4 sand + HP, there is a large crack causing a limestone aggregate particle to be completely debonded from the cement matrix (Figure 5.87I). There are some cracks in the cement matrix and only a few contain a brownish material. One example is observed in a rhyolite aggregate particle (Figure 5.87J). Some of the limestone particles present cracks with a brownish material and also in some cases the gel is outlining the particles. Brownish material is often either lining or partly filling the air voids.

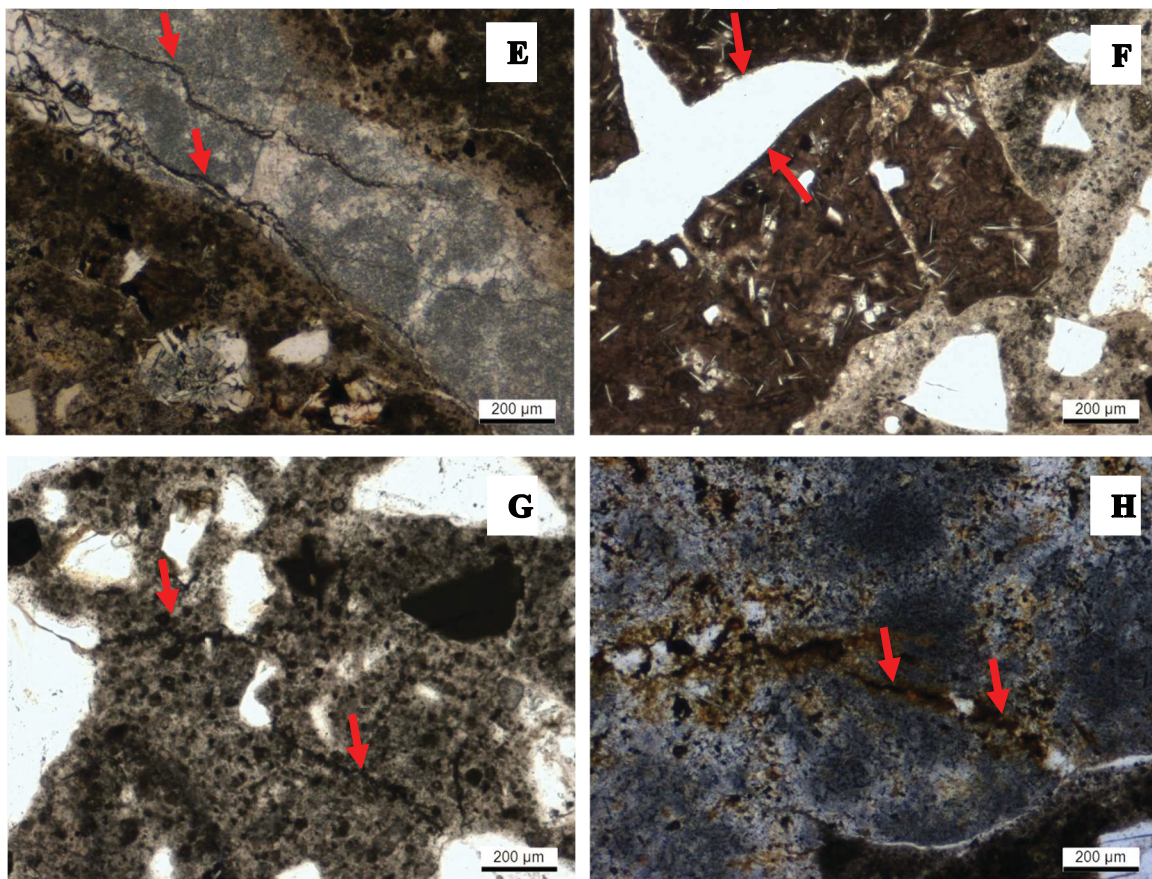


Figure 5.87 (continued). Photomicrographs of concrete prisms incorporating Icelandic aggregates. All photos are in PPL. E) Cracks in the limestone aggregate particle (ICL1 fine sand); F) Wide crack crossing a glassy basalt particle (ICL2); G) Crack in the cement matrix (ICL3); H) Crack inside a rhyolite aggregate particle (ICL4).



Figure 5.87 (continued). Photomicrographs of concrete prisms incorporating Icelandic aggregates. All photos are in PPL. I) Limestone aggregate particle debonded from the cement matrix (ICL4 sand); J) Crack starting in rhyolite aggregate particle and outlining other aggregate particles (ICL4 sand). The red arrows point to the cracks.

In the Icelandic concretes there is no clear evidence for an ongoing ASR, although in some cases it seems that something is happening in the rhyolite aggregate particles and in the darker basalt aggregate particles containing volcanic glass.

Japan

The concrete thin section confirms that the JAP aggregate is composed of andesite. The aggregate particles have an intergranular texture, with phenocrysts mainly of plagioclase, ortho- and clinopyroxene and opaque minerals. The groundmass contains plagioclase, clinopyroxene, silica minerals and opaque minerals.

In general, there are cracks in the cement matrix (Figure 5.88A) and some within the aggregate particles but they are mainly located near the border of the aggregate particles (Figure 5.88B and C). Others are surrounding the aggregate particles, which is debonded from the cement paste (Figure 5.88D). In both cases, the cracks are partly filled with brownish material or are empty. Regarding the air voids, some are lined with an isotropic brownish material.

The Japan concrete shows some evidence for an ongoing ASR.

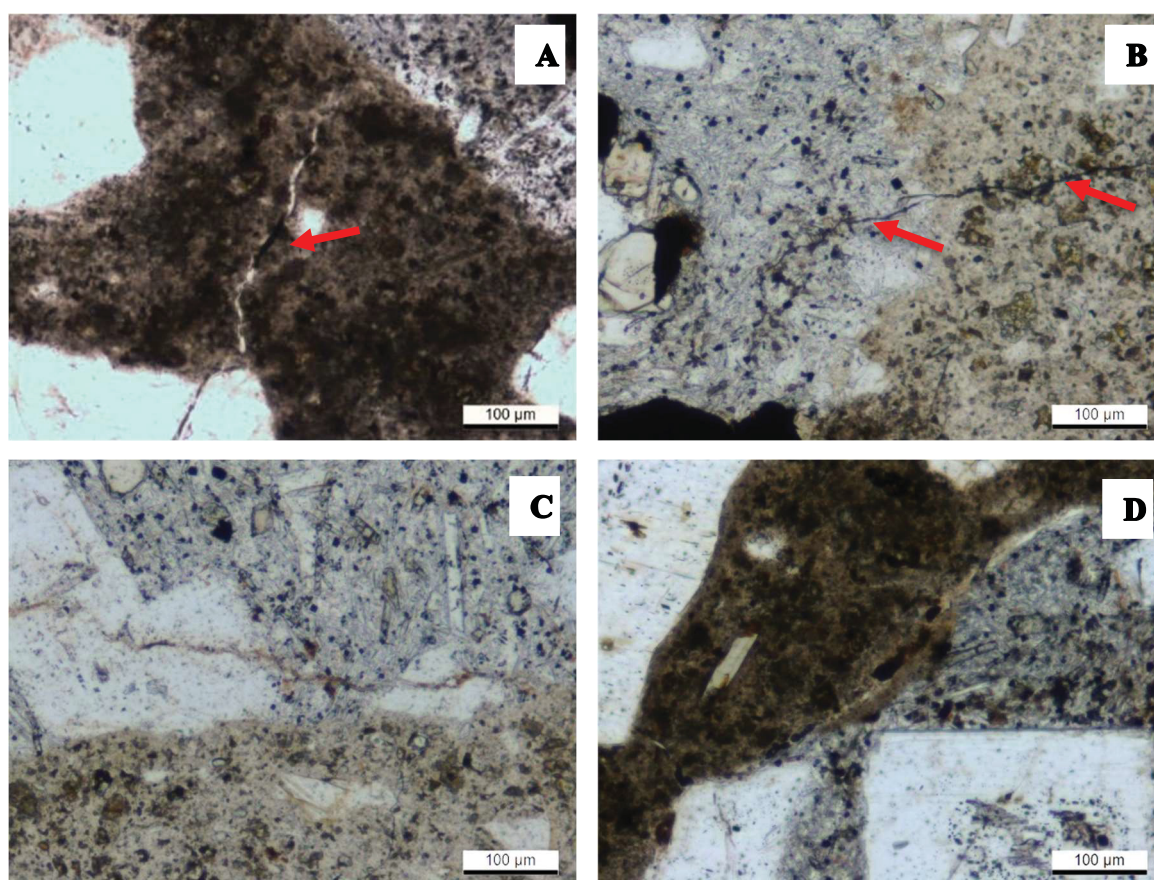


Figure 5.88. Photomicrographs of concrete prism incorporating the JAP aggregate. All photos are in PPL. A) Crack in the cement matrix with brownish gel, also cutting an aggregate particle; B) Crack inside an aggregate particle and in the cement matrix; C) Crack inside an aggregate particle but with no continuity into the cement matrix; D) Crack partly filled with brownish material surrounding the aggregate particle.

New Zealand

The concrete thin sections show that NZ2 and NZ3 aggregates are composed of basanite crushed rocks. In general, the aggregate particles have intersertal, intergranular and subophitic textures. The olivine phenocrysts are rimmed by iddingsite. The groundmass contains plagioclase, clinopyroxene, olivine, opaque minerals and brownish volcanic glass. Some aggregate particles appear with a very dark groundmass, probably with tachylite glass.

Both concrete thin sections with NZ2 and NZ3 aggregates show some cracks in the cement matrix, most of them being empty. There are only very few cracks partially filled by a brownish material (Figure 5.89A, B, C and D) and also some air voids are lined (Figure 5.89E and F) or filled by a brownish material.

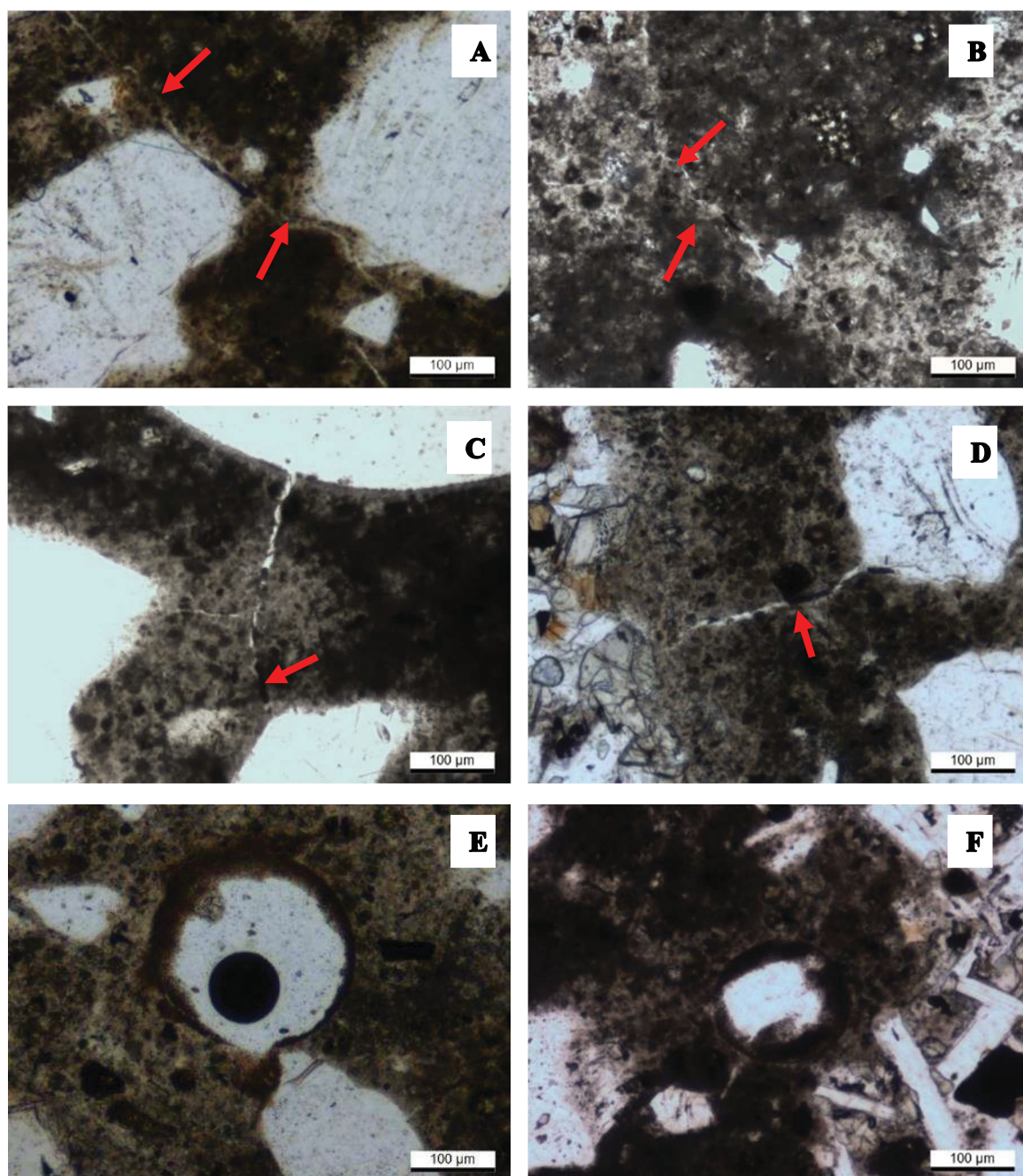


Figure 5.89. Photomicrographs of concrete prisms incorporating New Zealand aggregate. All photos are in PPL. A) Thin crack in the cement matrix (NZ2); B) Crack with brownish material in the cement matrix (NZ2); C) Cracks in the cement matrix, one with brownish material, connecting aggregate particles (NZ3); D) Crack with rare brownish material in the cement matrix (NZ3); E) Air void partly filled with a brownish material; F) Air void partly filled with a brownish material.

On the other hand, the aggregate particles have no cracks. In these two concrete thin sections, there are a few cracks with a brownish material but there is weak evidence for an ongoing ASR.

5.2. Sites/samples from Continental Regions

5.2.1. Geological setting

Brazil

Brazil is located on the eastern coast of South America washed by the Atlantic Ocean and occupies a large area. It borders most of the countries present in the continent (French Guiana, Suriname, Guyana, and Venezuela in the north; Colombia in the northwest; Peru and Bolivia in the west; Paraguay and Argentina in the southwest and Uruguay in the south) except for Ecuador and Chile. All coastline in the east is bordered by the Atlantic Ocean.

The basalt studied comes from Ilha Solteira in São Paulo state. This area is inserted in the Paraná-Etendeka Province (PEP) which was a single continental flood basalt province before South Atlantic rifting (Kirstein et al., 2000). The opening of the South Atlantic Ocean is marked by Mesozoic magmatism that spread throughout South America and SW Africa (Namibia and Angola) (Kirstein et al., 2000; Frank et al., 2009; Castanheira de Moraes et al., 2018). In South America, the Paraná Continental flood (Figure 5.90) is dispersed through southern Brazil (Rio Grande do Sul, Santa Catarina, Paraná, São Paulo, Mato Grosso do Sul, Minas Gerais and Goiás states), Uruguay, eastern Paraguay and northern Argentina (Misiones and Corrientes states) (Peate, 1990; Mincato, 2000). The volcanic rocks from the Paraná Province were formed in the last phase of the Paraná basin and are represented by the Formação Serra Geral (Castanheira de Moraes et al., 2018). These volcanic rocks are composed mainly of tholeiitic basalts and andesitic basalts and also several acid rocks (Tolloti, 2018) that include dacites and rhyolites with low-Ti content) and dacites with higher-Ti content (Castanheira de Moraes et al., 2018).

The Paraná basin itself is an intracratonic basin that was part of the Gondwana Continent (Castanheira de Moraes et al., 2018) and it was formed between the Ordovician and the Cretaceous (Frank et al., 2009; Tolloti, 2018). It is marked mainly by marine transgressions-regressions cycles and the magmatism of Serra Geral (Gondwana III) at the end of the Jurassic and the beginning of the Cretaceous (Tolloti, 2018). Overall, and according to Milani (1997), this volcanic-sedimentary sequence is composed of the following six super sequences: Rio

Ivaí, Paraná, Gondwana I, II and III and Baurú. The Serra Geral Formation is integrated in the Gondwana III supersequence.

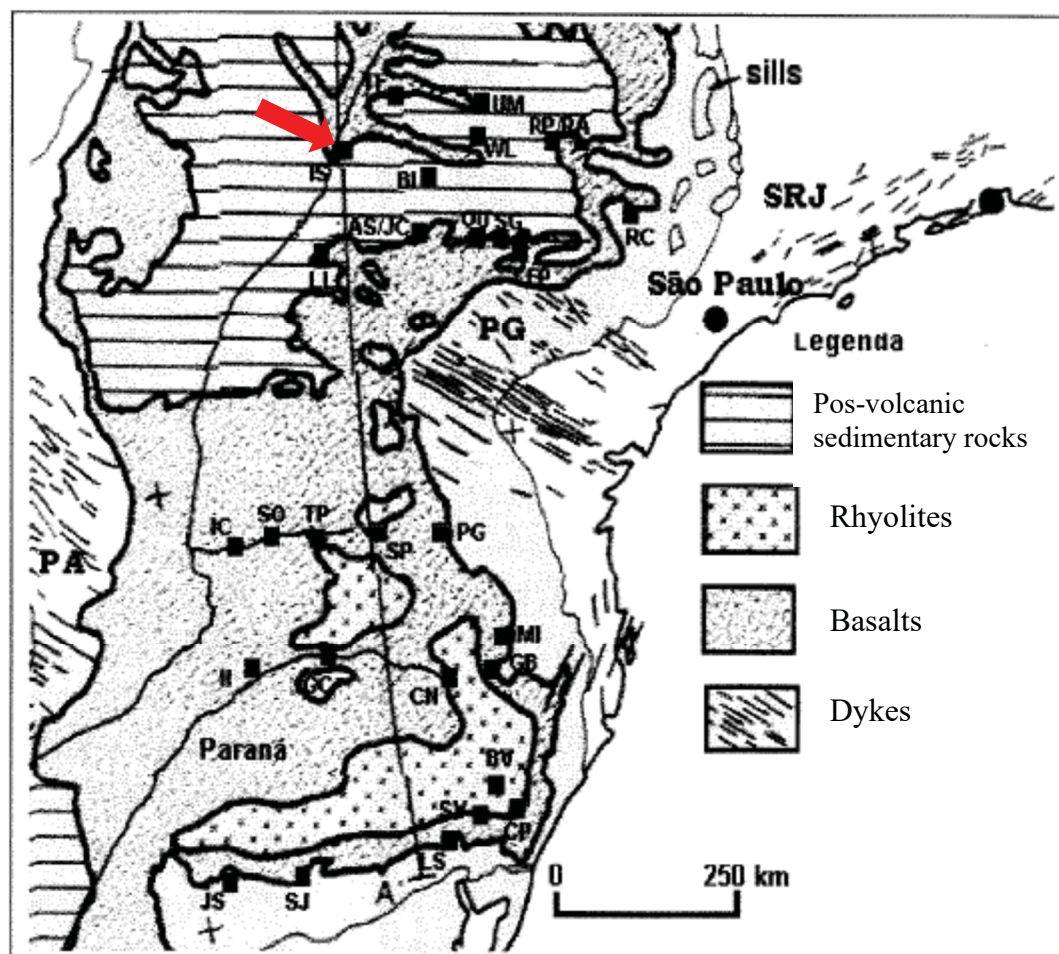


Figure 5.90. Map of the Paraná Continental flood (adapted from Mincato, 2000). The red arrow points to Ilha Solteira.

Canada

Canada is located in North America and extends from the Atlantic to the Pacific coastlines and in the north to the Arctic Ocean. It borders the United States of America in the south and in the east at about 20 km from Greenland (Denmark) in the northeast and Saint Pierre and Miquelon (France) in the southeast.

The basalt studied comes from the Quebec City area, in the Canadian Appalachian region. The Canadian part of the Appalachian region (Figure 5.91) includes Newfoundland, Nova Scotia, New Brunswick, Prince Edward Island, the southern part of Québec and the south side of the St. Lawrence River. The Appalachian region is a mountain belt or orogen from the Paleozoic age that was affected by folding, faulting, metamorphism and magmatism (Williams, 1995). The Appalachian orogen was formed by three sequential tectonic phases (Williams and

Hatcher, 1983): (1) Alleghanian orogeny (Carboniferous-Permian) restricted mainly to the Southern Appalachians, (2) Taconian orogeny (Middle/Late Ordovician) and (3) Acadian orogeny (Late Silurian/Middle Devonian), the last two being located in the Northern Appalachians.

Based on stratigraphic and structural contrasts with other rocks from other ages, the Appalachian orogen is divided into five zones, from west to east: Humber, Dunnage, Gander, Avalon and Meguma (Williams, 1979). The first three zones represent the generation and destruction of Iapetus Ocean: the Humber Zone represents the continental margin of Eastern North America in the west of Iapetus; the Dunnage Zone records the vestiges of Iapetus Ocean containing island arc sequences and “mélanges” built upon oceanic crust and the Gander Zone records the development and destruction of a continental margin. Castonguay et al. (2001) indicates that the Humber Zone is a rift-drift, continental passive margin.

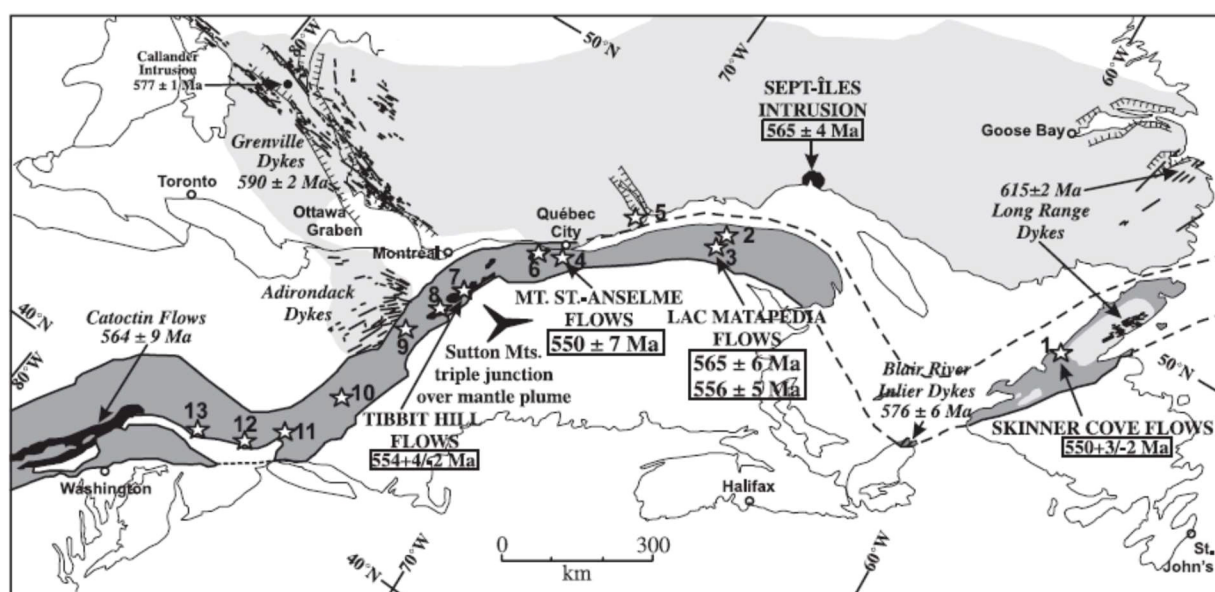


Figure 5.91. Map of the Appalachian orogeny in Canada and NE USA. The darker grey colour corresponds to the Humber Zone and light grey colour to the outcrops of the Grenville Province of cratonic Laurentia (Hodych and Cox, 2007). Ma: million of years

Williams (1995) indicates that the rocks of the Appalachian region contain discontinuous deep marine clastic and effusive volcanic units. The Humber zone is of Cambro-Ordovician age and includes the Montagne de Saint Anselme Formation that overlies unconformably the Grenville basement (La Flèche et al., 1993). This formation is formed by basaltic lava flows, intrusions and interbedded shallow-water sandstones (La Flèche et al., 1993; Hodych and Cox, 2007) from late Neoproterozoic age (Hodych and Cox, 2007). This sequence is interpreted as

a continental rift, marking the opening of Iapetus Ocean, the precursor of the Atlantic Ocean (Iapetus) (La Flèche et al., 1993; Hodych and Cox, 2007). According to Valéries et al. (1978) the Montagne de Saint-Anselme Formation constitutes a precursor to the filling of the Appalachian mobile belt, where lava flows represent the products of early-rifting. These lava flows are of alkaline character according to several authors (e.g. Valéries et al., 1978; La Flèche et al., 1993), or with tholeiitic affinity, according to others (e.g., Malo et al., 2008).

Mozambique

Mozambique is located in the southeast of the African Continent, bordering with Tanzania in the north, Malawi and Zambia in the northwest, Zimbabwe in the west, Swaziland in the southwest, South Africa in the southwest and south and Madagascar Island is to the east, at a distance of about 416 km in the Indian Ocean, which borders all the east coast of Mozambique.

The rhyolite studied comes from the unit of Lebombo Monocline. The Lebombo Monocline is a 600 km long and 5–30 km wide linear flexure (Miller and Harris, 2007) located along the boundary between South Africa and Mozambique (Manninen et al., 2008) (Figure 5.92). It is part of the volcanic rocks of the regional Karoo Large Volcanic Province (KLIP) (Figure 5.92) together with the Nuanetzi-Sabi Monocline. Both monoclines can be considered as volcanic rift type large cracks that mark the eastern margin of the Kaapval and Zimbabwe cratons (GTK Consortium, 2006). But according to Manninen et al. (2008), the Nuanetzi-Sabi volcanic flexure is an extension of the Lebombo Monocline and represents one of the rift arms of the Limpopo triple junction structure. This type of structure is also mentioned in GTK Consortium (2006) and is known as a mantle diapir triple junction (e.g. the Lebombo-Nuanetzi-Limpopo triple junction). That three structurally controlled belts meet near Pafuri located at the border with Zimbabwe, and: (1) the northern NNE-SSW to NE-SW belt is represented by the Nuanetzi-Sabi volcanic flexure; (2) the NNW-SSE to N-S belt is represented by the Lebombo Monocline, and (3) the third branch of volcanic rocks has been developed, with a E-W trend and extends towards the WNW-ESE trending Okavango dyke swarm (Figure 5.92).

The volcanic rocks of Lebombo belong to the final phase of the Karoo Supergroup (Melluso et al., 2008) which ranges in age from Late Carboniferous to Early Jurassic and is divided into Upper Karoo and Lower Karoo Groups. It represents the Karoo event, which is referred to the break-up or rift phase of the Gondwana supercontinent and is characterized by the development of intracratonic tectonic pits and deep basins, and on a later phase with the installation of the Great Karoo Igneous Province, of lower Jurassic age (~ 190 my.) (GTK Consortium, 2006).

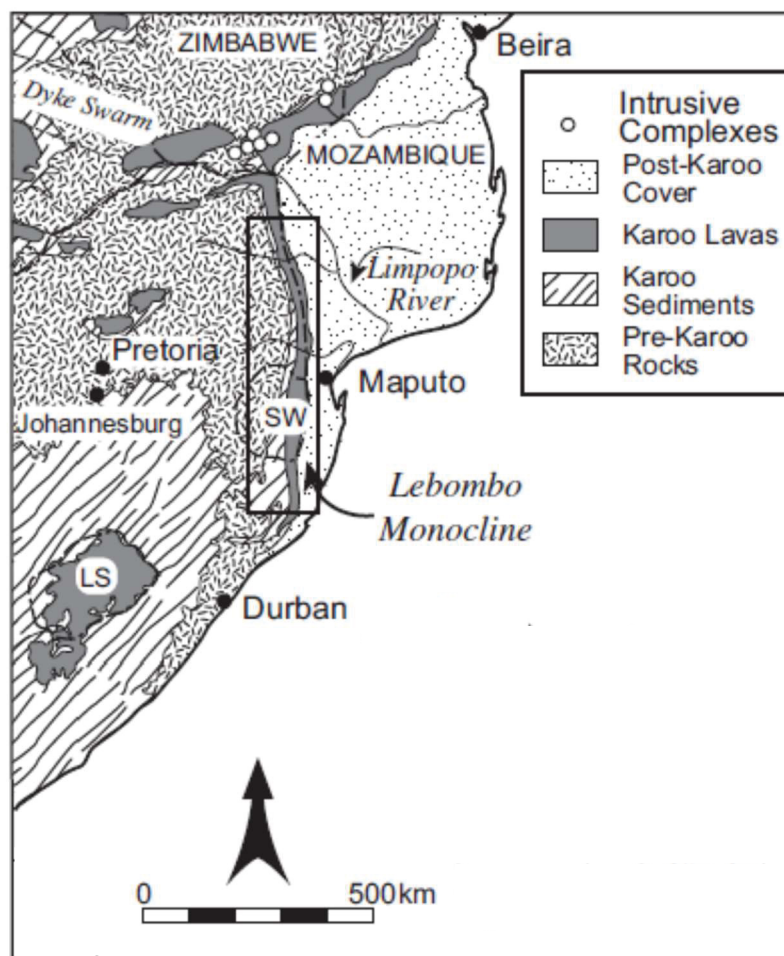


Figure 5.92. Simplified geological map of south-eastern Africa (Miller and Harris, 2006).

The Lebombo Monocline is characterized by pulses of mafic and felsic volcanism; the rhyolites form the “Great” (Grandes) and the “Little” (Pequenos) Lebombo mountains are interlayered with the Movene basalts (Manninen et al., 2008). Overall, Lebombo is characterized by ultra-potassic volcanism that is represented by nephelinites and by picritic and high (Ti, Zr) basaltic lavas and subsequently by volcanic rocks of bimodal composition, containing tholeiitic intraplate basalts and rhyolites, those with a calc-alkaline trend (GTK Consortium, 2006).

Norway

Norway is located in the northern Europe and occupies the western and northernmost part of the Scandinavian Peninsula. At northeast, Norway is bordered by Russia and Finland and by Sweden at east. All coastlines, at north and west, are bordered by the Atlantic Ocean and the Barents Sea and by the North Sea at south.

The sample studied from Norway comes from Steinskogen, west of Oslo. It consists of a basalt from the Bærum caldera, considered a part of the Oslo Graben, a NNE-SSW trend graben system that was largely formed in Permo-Carboniferous (Rallakis, 2013).

The Oslo area is essentially controlled by a NNE-SSW trend graben system that was largely formed in Permo-Carboniferous (Rallakis, 2013). The Oslo Graben is a major structure representative of the Oslo rift on land (Nilsen, 1992). This is a continental rift system (Nilsen, 1992; Neumann et al., 2006) of Permo-Carboniferous age that was active for more than 60 million years with several intrusive and volcanic periods (Nilsen, 1992). The rift consists of a series of graben segments, and in general terms the Oslo graben includes two asymmetric graben segments bounded by roughly N-S trending faults: the Vestfold graben segment in the south and the Akershus in the north (Neumann et al., 2006; Rallakis, 2013). But seen in more detail perspective, the segments are the Akershus, Rendalen and Vestfold grabens in the north (onshore) and the Skagerrak graben (offshore) in the south (Rallakis, 2013). Six stages have been considered for the evolution of the Oslo rift (Corfu and Dahlgren, 2008): (1) Proto-rift stage, with deposition mainly of fluvial and lacustrine sediments; (2) initial basalt stage, with emplacement of microsyenite sills and dykes and by alkaline to tholeiitic basaltic volcanism; (3) main plateau lava flows and rift valley stage, with extensive vertical movements and extensive eruptions of trachyandesitic rhomb porphyry lavas; (4) central volcano and caldera-forming stage, with formation of central volcanoes, caldera collapse and graben fill; (5) syenitic batholiths stage, with emplacement of mainly syenitic to granitic batholiths and (6) termination stage with two granitic intrusions (Rallakis, 2013).

Regarding the Bærum Cauldron (Figure 5.93), it is one of the best preserved caldera structures of the Oslo rift (Nilsen, 1992). It forms an elliptical block that sank down inside a ring fault along which a nordmarkitic (e.g., variety of syenite) to granitic dike was emplaced (Smithson, 1961). Different lithologies surround this caldera (Smithson, 1961; Nilsen, 1992): larvikitic (i.e. variety of syenite or monzonite) plutons in the north; nordmarkitic plutons with some granite in the east; Cambro-Silurian limestones and shales from Cambro-Silurian and sandstone from Lower Devonian in the south and a basaltic and rhomb porphyry lava flows from Permian age forms the Krokskogen lava plateau, in the west. The subsided block is formed by a layered sequence of lava flows and conformable felsite intrusions or ignimbrites. These lava flows are composed of basalt (B3) metamorphosed and rhomb porphyries and trachytes (Smithson, 1961).

A sequence of events occurred in the Palaeozoic (Rallakis, 2013): (1) during the Cambro-Silurian period, marine sediments were deposited in an epicontinental sea environment; (2) sandstones from Upper Silurian were deposited in a foreland basin and, during Permo-

Carboniferous, thick lava flows were spread on top of the sedimentary rocks or formed calderas and lava plateau throughout the rift episodes.

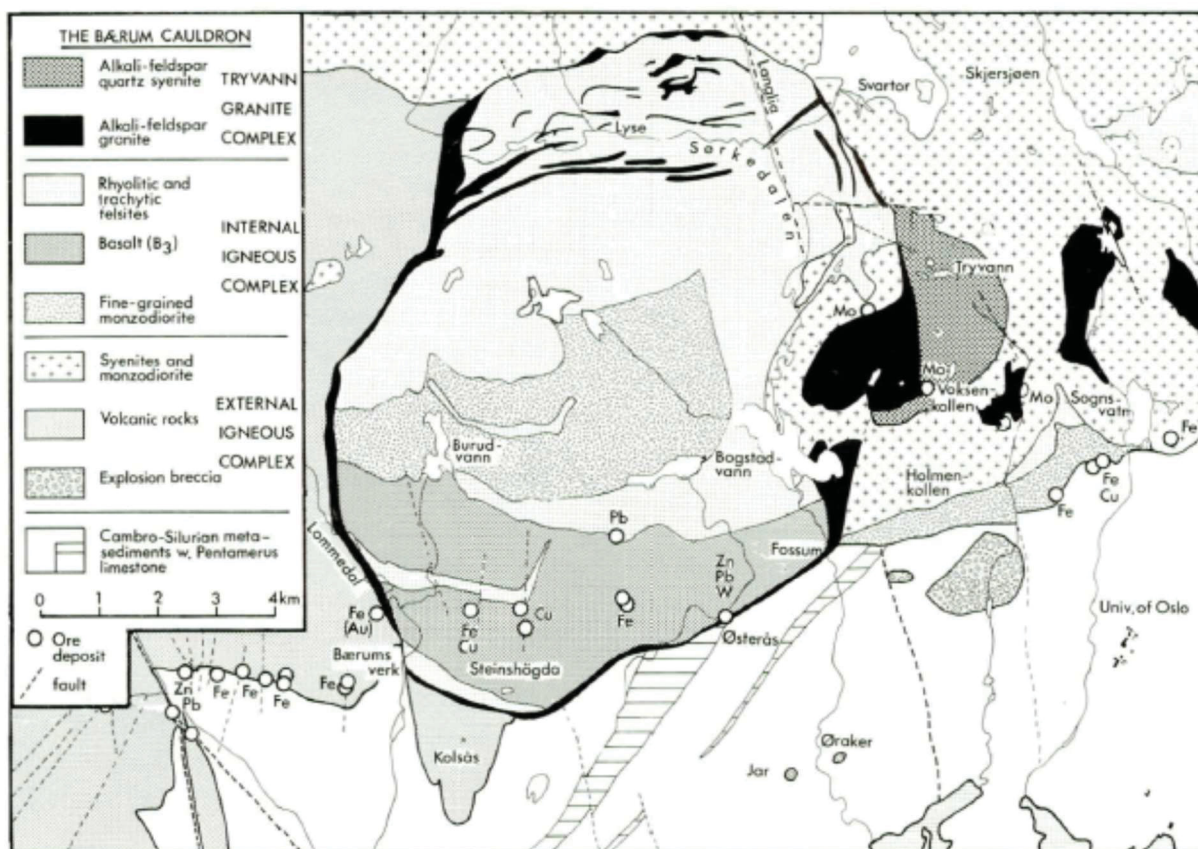


Figure 5.93. Geological map of Bærum Caldron (Nilsen, 1992).

Turkey

Turkey makes the border between the southeastern Europe and Western Asia. Different countries border Turkey: Greece and Bulgaria in the northwest; Syria and Iraq in the south; Iran, Azerbaijan and Armenia in the east and Georgia in the northeast. All north coast is bordered by the Black Sea, part of the south coast is border by the Mediterranean Sea and the east coast by the Aegean Sea.

The andesite studied comes from the Bozdivlit Mountain, Çaltılıdere, Aliağa, western Turkey. Based on a report from the Turkish General Directorate of Mineral Research and Exploration (MTA), Çopuroğlu et al. (2009) and Fernandes and Andiç-Çakır (2015) report that the regional geology defines the rock units from this area as Bozdivlit andesitic basalts, being very thick at Bozdivlit Mountain (Albayrak and Özgüner, 2013). Also, the first two authors mention that in previous works, the Upper Miocene rocks have been designated as basalt, basaltoid, and/or basaltic andesite. According to Tunçel (2021), the Bozdivlit Hill is a volcanic peak that was formed during the Miocene period (Figure 5.94).

The Bozdivlit andesitic basalts (Tba), along with the Hatundere dacites (Tdst), Sarıkaya rhyolites (Tryl) and Dumanlıdağ andesites (Tand), overlie the Miocene Aliğa pyroclasts (Tap). Those rocks have a calc-alkaline character and form short and thick lava flows (Anadolou, 2011).

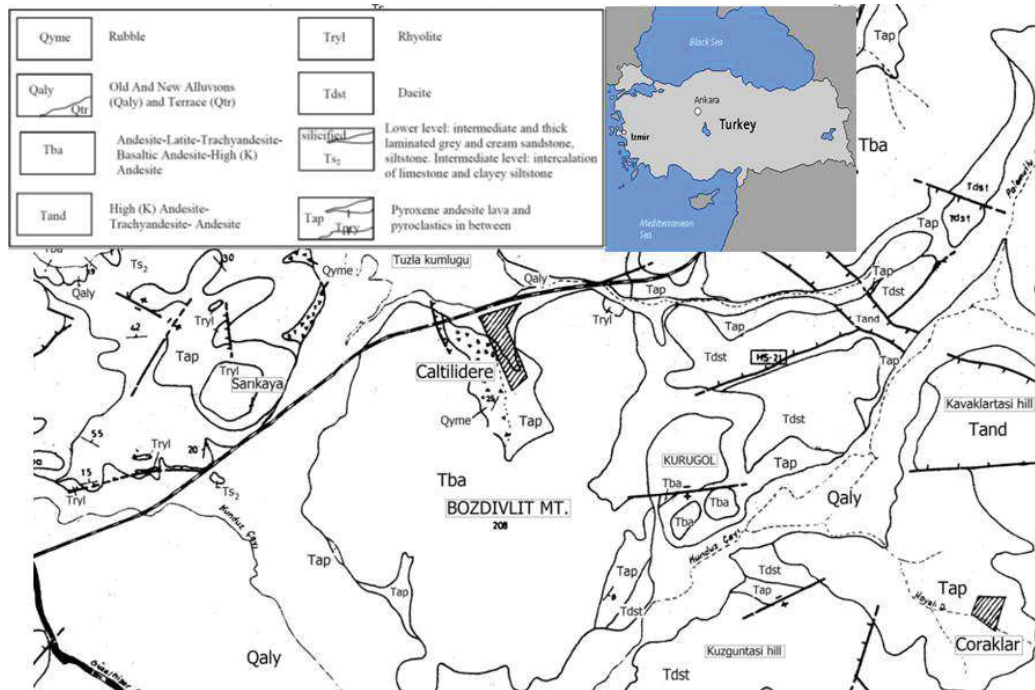


Figure 5.94. Geological map of the Bozdivlit andesitic basalts area, Turkey (Fernandes and Andiç-Çakır, 2015).

This area is located in western Anatolia where magmatism has played an important role. Akay and Erdoğan (2004) describe three models that have been proposed to explain the tectonic and magmatic evolution in this area: (1) a N–S-directed extensional tectonic regime and associated magmatism that was controlled by this extensional regime during Late Oligocene; (2) magmatism that was generated by the northward dipping subduction of the eastern Mediterranean oceanic floor along the Hellenic Trench, and (3) during the Late Oligocene-Middle Miocene period, a N–S compression occurred that resulted in a WNW–ESE directed extensional regime and NE–SW-trending weakness zones along which the calc-alkaline magmatism took place; from the end of Miocene-Pliocene to recent times, a N-S extension has been activated and produced alkaline magmatism associated with E-W trending graben structures.

5.2.1. Characterization of volcanic aggregates from continental regions

5.2.2.1. Geochemical analysis, TAS diagram and CIPW norm

Geochemical analyses of the aggregates from the continental regions were performed at the Activation Laboratories (ACTLABS), in Canada, by using the lithium metaborate/tetraborate fusion–ICP and ICP/MS method. Table 5.29. shows the results obtained. The results were also plotted in a TAS diagram (Le Bas et al., 1986) by using the free software GCDKit3.00.

Table 5.29. Bulk chemical composition of the continental volcanic aggregates.

Major Oxides (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ total	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	SUM total
BRAZ	48.92	13.11	14.38	5.64	9.82	2.46	0.99	2.01	0.21	0.21	1.90	99.77
CAN	45.56	13.60	12.37	6.32	10.45	3.95	0.59	1.63	0.17	0.19	4.90	99.81
MOZ	77.69	10.79	2.10	0.09	0.23	2.45	5.06	0.17	0.01	0.01	1.20	99.98
NOR	44.19	13.47	13.94	7.64	9.28	2.41	1.59	3.06	0.45	0.01	3.40	99.77
TK	60.20	16.01	5.29	3.39	6.12	2.56	2.46	0.63	0.16	0.09	2.10	99.92

The chemical composition of the aggregates from continental regions shows some differences regarding the content in SiO₂ and LOI. The SiO₂ content of BRAZ, CAN and NOR is lower than 50%, ranging between 44.19% to 48.92% with the exception of the samples of MOZ (77.69%) and TK (60.20%), which are more evolved rocks.

Regarding LOI, the highest contents are found for CAN (4.9%) and NOR (3.4%), indicating that there is some alteration of the rocks.

According to Yoder and Tilley (1962) and based on the results of the calculation of the CIPW norm (Table 5.30), the sample from Brazil is considered a basalt undersaturated in silica, as it contains normative hypersthene and olivine, while the samples from Canada and Norway are alkali basalts because they have both normative nepheline and olivine.

Table 5.30. Results of the calculation of the continental volcanic aggregates CIPW norm (wt %).

Normative minerals	Q	Pl	Or	Ne	Di	Crn	Hy	Ol	Ac	Il	Mt	Ap	Total
BRAZ	0.0	43.55	5.97	0.0	21.85	0.0	17.00	5.49	0.0	3.89	1.74	0.49	99.98
CAN	0.0	38.26	3.66	8.42	28.95	0.0	0.0	15.41	0.0	3.27	1.62	0.42	100.0
MOZ	42.77	22.06	30.32	0.0	0.0	0.91	3.16	0.0	0.0	0.32	0.41	0.02	99.97
NOR	0.0	38.79	9.75	2.42	18.78	0.0	0.0	21.51	0.0	6.04	1.57	1.09	100.0
TK	16.14	48.04	15.01	0.0	3.71	0.0	14.75	0.0	0.0	1.23	0.72	0.39	99.99

Q=quartz; Pl=plagioclase; Or= Orthoclase; Ne=Nepheline; Di= Diopside; Hy=Hypersthene; Ol=Olivine; Ac=Acmite; Il=Ilmenite; Mt=Magnetite; Ap=Apatite; Crn= corundum

The alkali-silica diagram (TAS) (Figure 5.95), shows that the volcanic rocks studied from the continental regions are basalts, one andesite and one rhyolite.

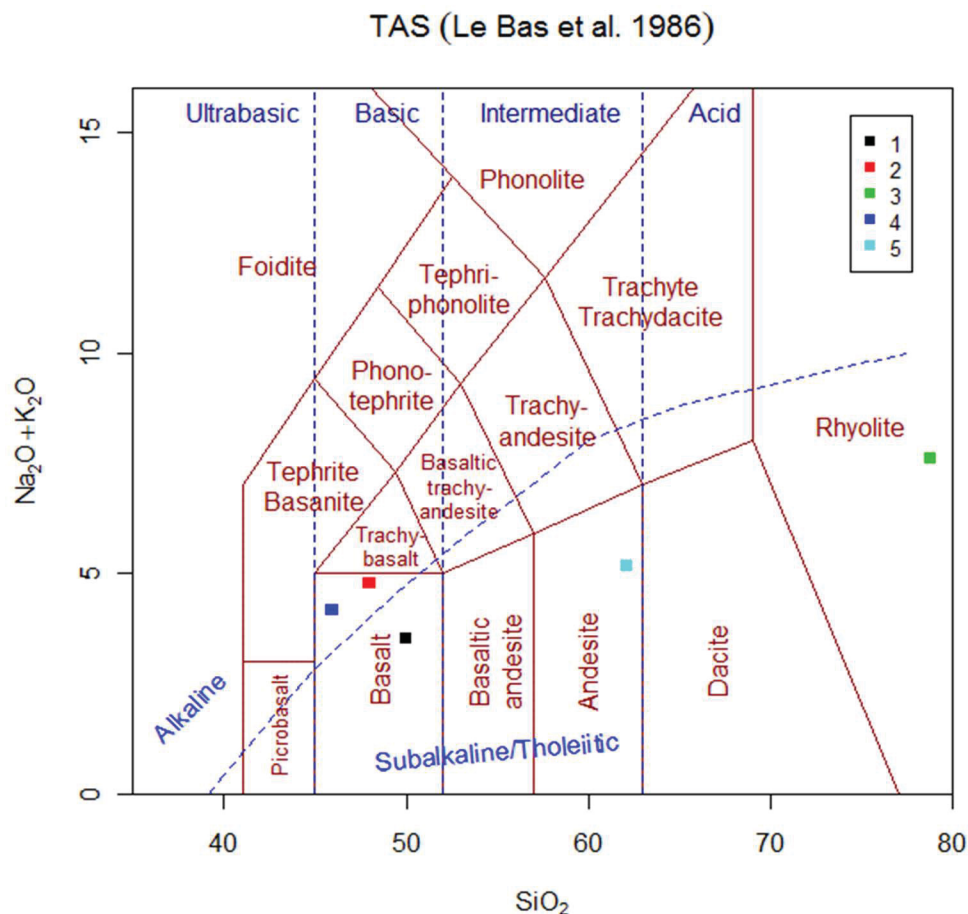


Figure 5.95. TAS diagram (after Le Bas et al., 1986) of the volcanic aggregates from continental regions: 1 - Brazil, 2 - Canada, 3 - Mozambique, 4 – Norway and 5 - Turkey.

The other two samples are one rhyolite (MOZ) and one andesite (TK). The chemical classification of the rocks obtained by the TAS diagram is summarized in Table 5.31.

From the TAS diagram, it is also possible to classify the rocks into alkaline or subalkaline/tholeiitic magma series. The rocks studied from Canada and Norway belong to the alkaline series as already mentioned. The other three samples fall in the subalkaline/tholeiitic magma series. According to the AFM diagram from Irvine and Baragar (1971), only the Brazilian sample belongs to the tholeiitic series, the rest of the samples follow a calc-alkaline trend (Figure 5.96).

Table 5.31. Chemical classification of each rock sample based on the TAS diagram.

Country	Sample	Chemical classification
Brazil	BRAZ	Basalt
Canada	CAN	Basalt
Mozambique	MOZ	Rhyolite
Norway	NW	Basalt
Turkey	TK	Andesite

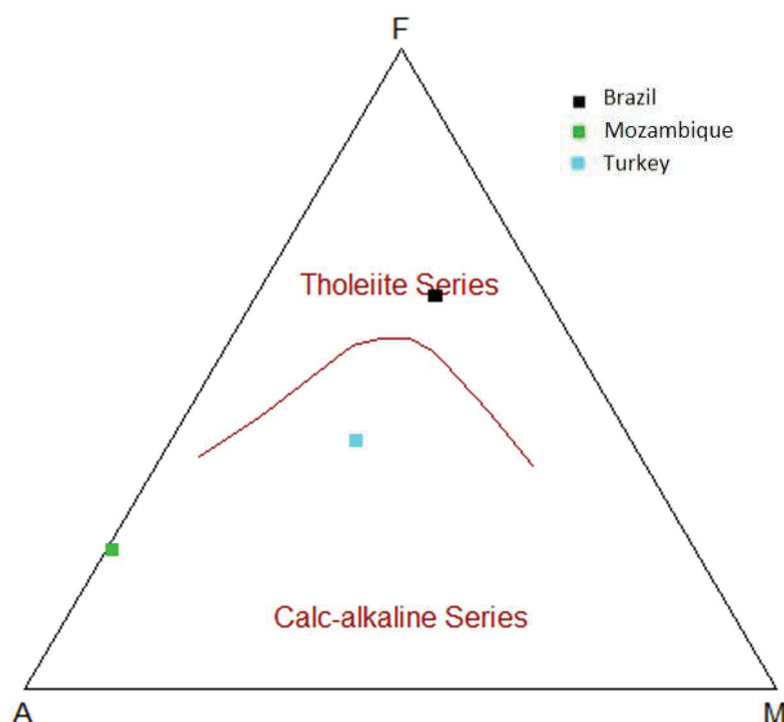


Figure 5.96. AFM diagram (after Irvine and Baragar, 1971) of the continental volcanic aggregates studied where BRAZ (Brazil) follows a tholeiitic trend, MOZ (Mozambique) and TK (Turkey) a calc-alkaline trend. A = Na₂O + K₂O; F = FeO + 0.8998 Fe₂O₃; M = MgO (wt.%).

5.2.2.2. Petrographic examination

Brazil

Macroscopically, the crushed aggregate sample from Brazil is aphyric with a brownish-grey colour and sub-angular particles (Figure 5.97A and B). Some of the aggregate particles show a reddish surface, others contain some white material not reactive with HCL and others are whitish particles similar to quartz (Figure 5.97B), which may be part of a silica vein. Figures 5.97 (A and B) show the different fractions and the detail of the one that contains white particles or basaltic particles with a surface with a white material.



Figure 5.97. Macroscopic photos of the BRAZ aggregate divided in different fractions. A) General view; B) detail of the fraction with white particles.

In thin section, BRAZ sample has mostly a subophitic texture and is mainly composed of subhedral plagioclase and clinopyroxene minerals. Intergranular to intersertal textures are also present. Phenocrysts of plagioclase and clinopyroxene are observed in some of the aggregate particles. Also, celadonite (green) with a micaceous texture is scattered throughout the rock (Figure 5.98A), sometimes associated with silica minerals (confirmed by EMPA) forming radial texture (Figure 5.98B).

Quartz shows undulose extinction. Also, a yellowish-green or greenish material is dispersed in irregular patches and occupies large areas in the rock. It shows radial fibrous structure and is anisotropic, especially in the rims, and isotropic towards the center seem (Figure 5.98C and D). These optical characteristics are compatible with chlorophaeite. Beige volcanic glass (Figure 5.98E) and green glass are also present in different areas of the rock. Opaque minerals are dispersed all over the different aggregate particles, sometimes forming skeletal texture. Calcite occurs both filling a vein and partially replacing plagioclase crystals. The white aggregate particles are formed by grains of quartz and fibrous chalcedony (Figure 5.98F). EMPA analyses were performed aiming at the identification of minerals and volcanic glass. Volcanic glass occurs as brownish, yellowish-green and green material scattered in the groundmass (Figure 5.99A, B1 and B2; Table 5.32), and possibly chlorophaeite that corresponds to green to brown material (Figures 5.100 A and B, Figures 5.101A1 and A2, Tables 5.33, 5.34), sometimes replacing olivine. Silica minerals (Figure 5.101B1 and B2; Table 5.34) were also identified.

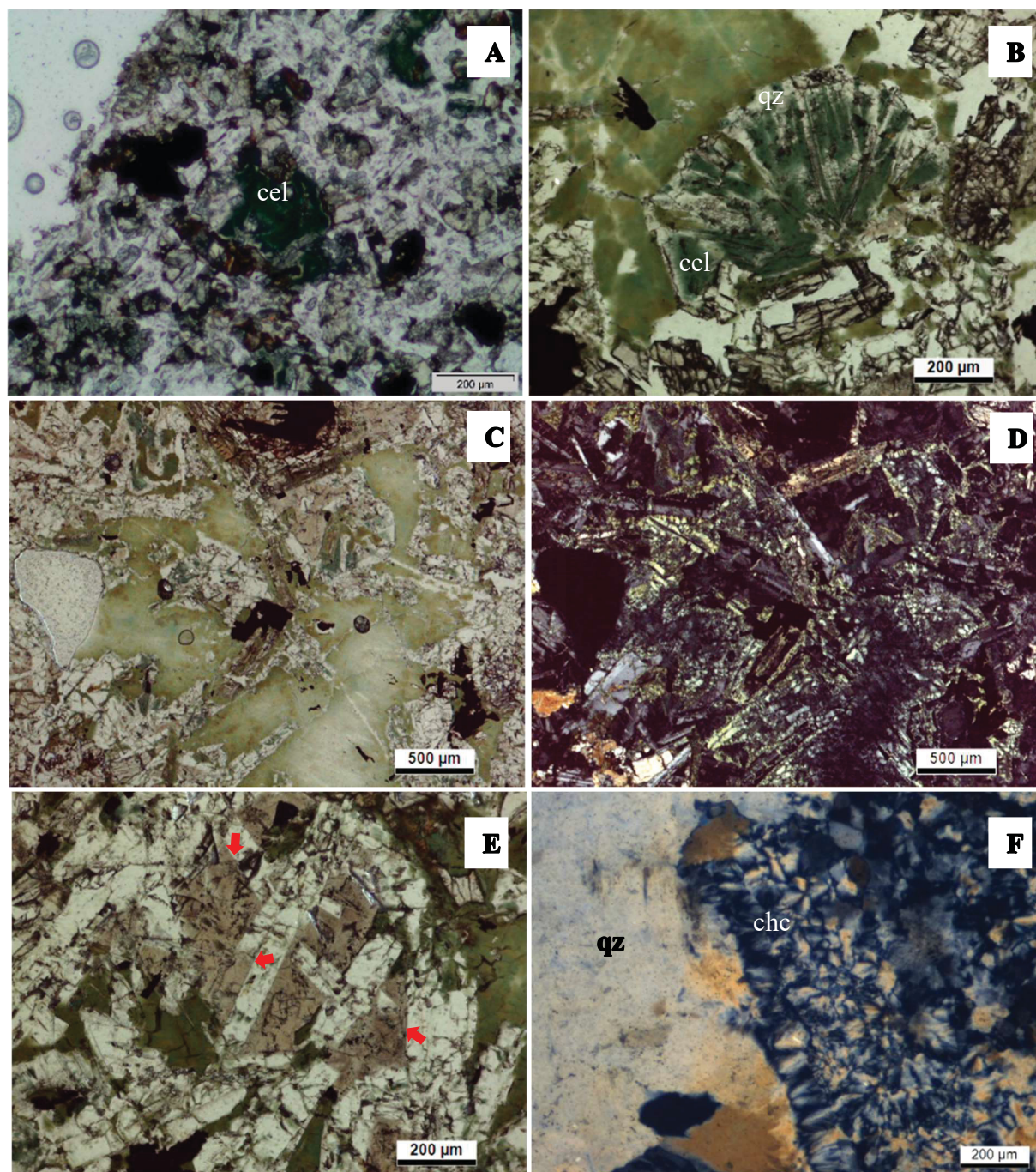


Figure 5.98. Photomicrographs of BRAZ sample: D and F in XPL, A, B, C and E in PPL. A) Green celadonite (Cel); B) Green celadonite (cel) associated with quartz (qz) forming radial texture; C) greenish material in PPL and D) the same material in XPL showing anisotropic radiating fibrous structures; E) Beige volcanic glass (red arrows); F) Aggregate particle composed of quartz (qz) and chalcedony (chc).

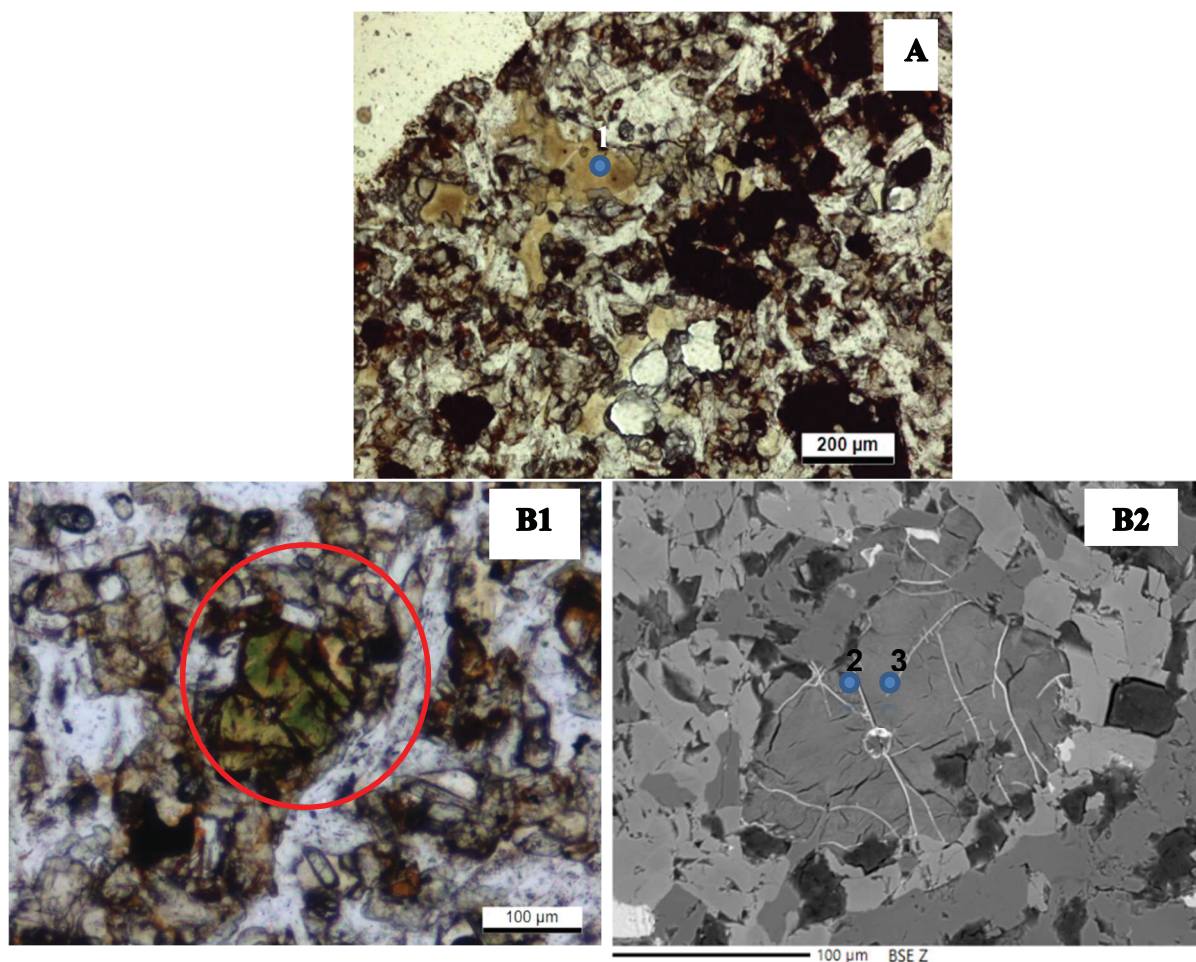


Figure 5.99. Basalt in BRAZ-F1 sample. Photomicrograph (A and B1) in PPL and BSE image (C2) showing the points of analysis.

Table 5.32. Sample BRAZ-F1. EPMA indicative results of volcanic glass in BRAZ-F1 sample.

Oxides (%)	1	2	3
SiO ₂	54.86	53.32	54.36
TiO ₂	-	0.14	0.15
Al ₂ O ₃	8.25	5.40	6.12
FeO	20.76	21.19	19.85
MnO	-	0.11	0.12
MgO	4.76	4.97	5.30
CaO	1.96	1.06	1.27
Na ₂ O	b.d.l.	b.d.l.	0.05
K ₂ O	1.73	5.99	5.57
Total	92.31	92.19	92.83
b.d.l. = below detection limit			

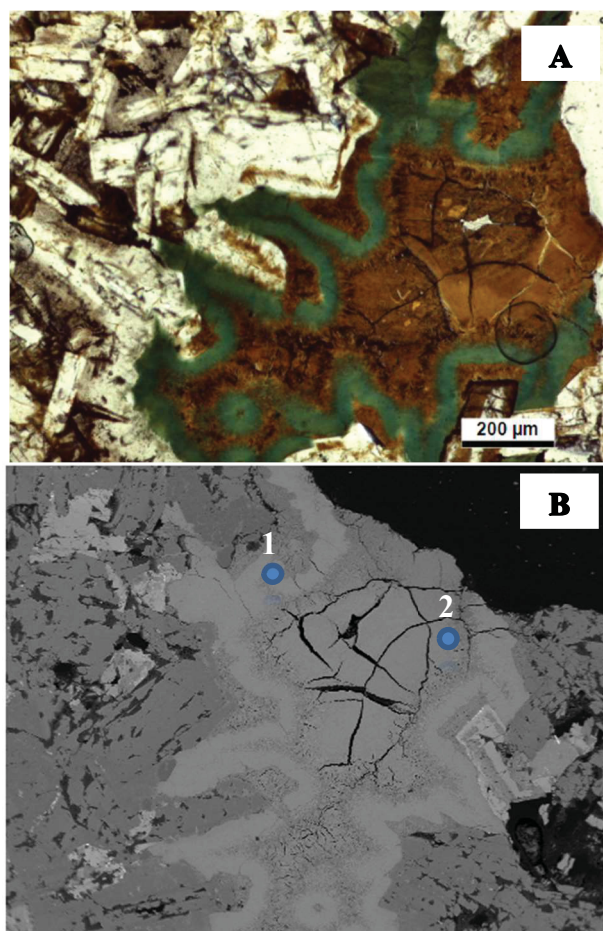


Figure 5.100. Sample BRAZ-F2 (Basalt). Photomicrograph (A) in PPL and BSE image (B) with respective points of analysis.

Table 5.33. Sample BRAZ-F2. EMPA results of possibly chlorophaeite (?) (1 and 2).

Oxides (%)	1	2
SiO ₂	54.43	53.89
TiO ₂	b.d.l.	b.d.l.
Al ₂ O ₃	2.56	2.56
FeO	20.99	20.09
MnO	b.d.l.	0.02
MgO	5.79	6.23
CaO	0.38	0.36
Na ₂ O	b.d.l.	b.d.l.
K ₂ O	8.89	9.01
Total	92.98	92.14

b.d.l. = below detection limit

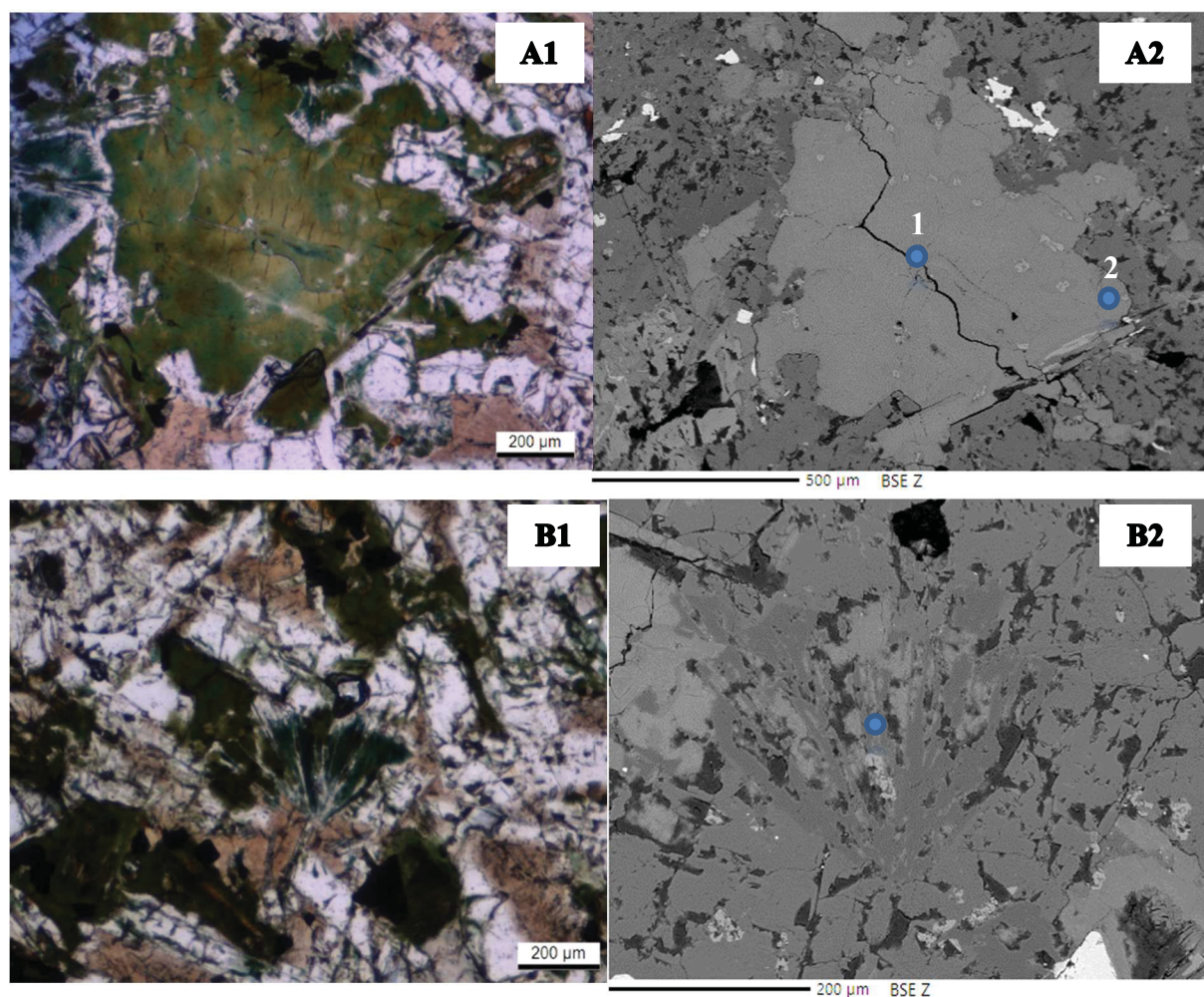


Figure 5.101. Basalt in BRAZ-F2. Photomicrograph (A1, B1) in PPL and BSE image (A2, B2) and respective points of analysis.

Table 5.34. Sample BRAZ-F2. EMPA results of possibly chlorophaeite? (1-2) and silica minerals (3).

Oxides (%)	1	2	3
SiO ₂	54.06	53.03	97.68
TiO ₂	-	0.12	-
Al ₂ O ₃	3.95	4.76	0.55
FeO	23.93	23.36	0.29
MnO	b.d.l.	b.d.l.	-
MgO	3.92	3.78	-
CaO	0.28	0.34	0.06
Na ₂ O	b.d.l.	b.d.l.	0.19
K ₂ O	8.11	7.90	0.08
Total	94.26	93.32	98.80

b.d.l. = below detection limit

Canada

From the macroscopic point of view, CAN crushed aggregate is aphanitic with some surfaces showing reddish or greenish tones (Figure 5.102). The particles show angular to subangular forms, some have elongated shape. The aggregate particles are massive, only punctuated by white small crystals filling vesicles or by white veinlets. The aggregate samples were separated by fractions based on texture and colour.

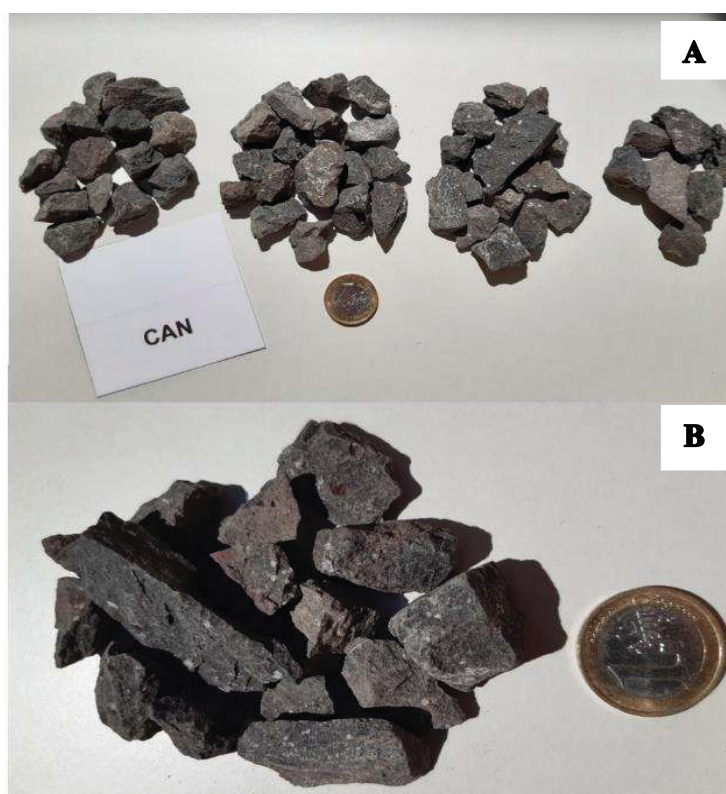


Figure 5.102. Macroscopic photos of the CAN aggregate with different fractions: A) General view; B) detail of one of the fractions containing white minerals.

In thin section, CAN sample shows intergranular and subophitic textures and is mainly composed of altered plagioclase and clinopyroxene (e.g. augite) minerals (Figure 5.103A). In one of the particles, the groundmass contains dendritic fans of clinopyroxene and some skeletal plagioclase. Glomeroporphyritic clusters of plagioclase and clinopyroxene are also observed. The plagioclase appears in subhedral crystals with some degree of alteration while augite does not seem to be altered or is less altered (Figure 5.103B). The plagioclase phenocrysts are being replaced by chlorite and calcite, which are present either replacing other minerals or filling vesicles (Figure 5.103C and D). Calcite occurs also in some veins in the rock (Figure 5.103E) or at the border of the aggregate particles. Opaque minerals are ubiquitous in the rock. Volcanic glass was also observed filling vesicles (Figure 5.103F).

Further analysis was done by EPMA, in order to identify some of the minerals and the volcanic glass. Green volcanic glass was identified filling vesicles (Figures 5.104 and Figure 5.105) and confirmed by the chemical composition in Tables 5.35 and 5.36. In Figure 5.104 A1 and A2, pyroxene could only be identified by the chemical composition obtained in Table 5.35.

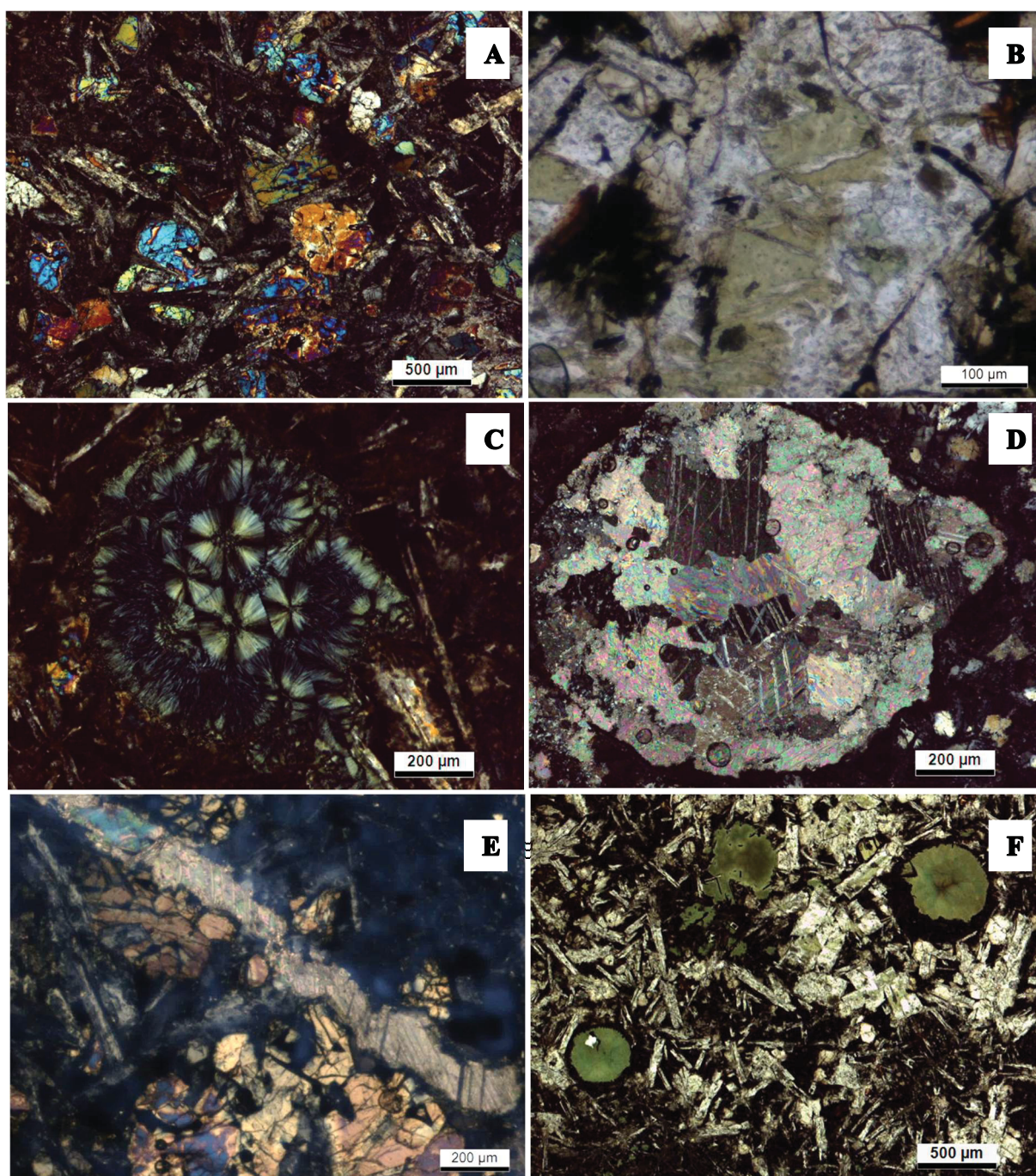


Figure 5.103. Microphotographs of CAN sample. Photo A, C, D and E in XPL. Photos B and F in PPL. A) Subophitic texture; B) Plagioclase being altered in green chlorite; C) vesicle with chlorite; D) Vesicle filled with calcite; E) Vein of calcite; F) Green volcanic glass in vesicles.

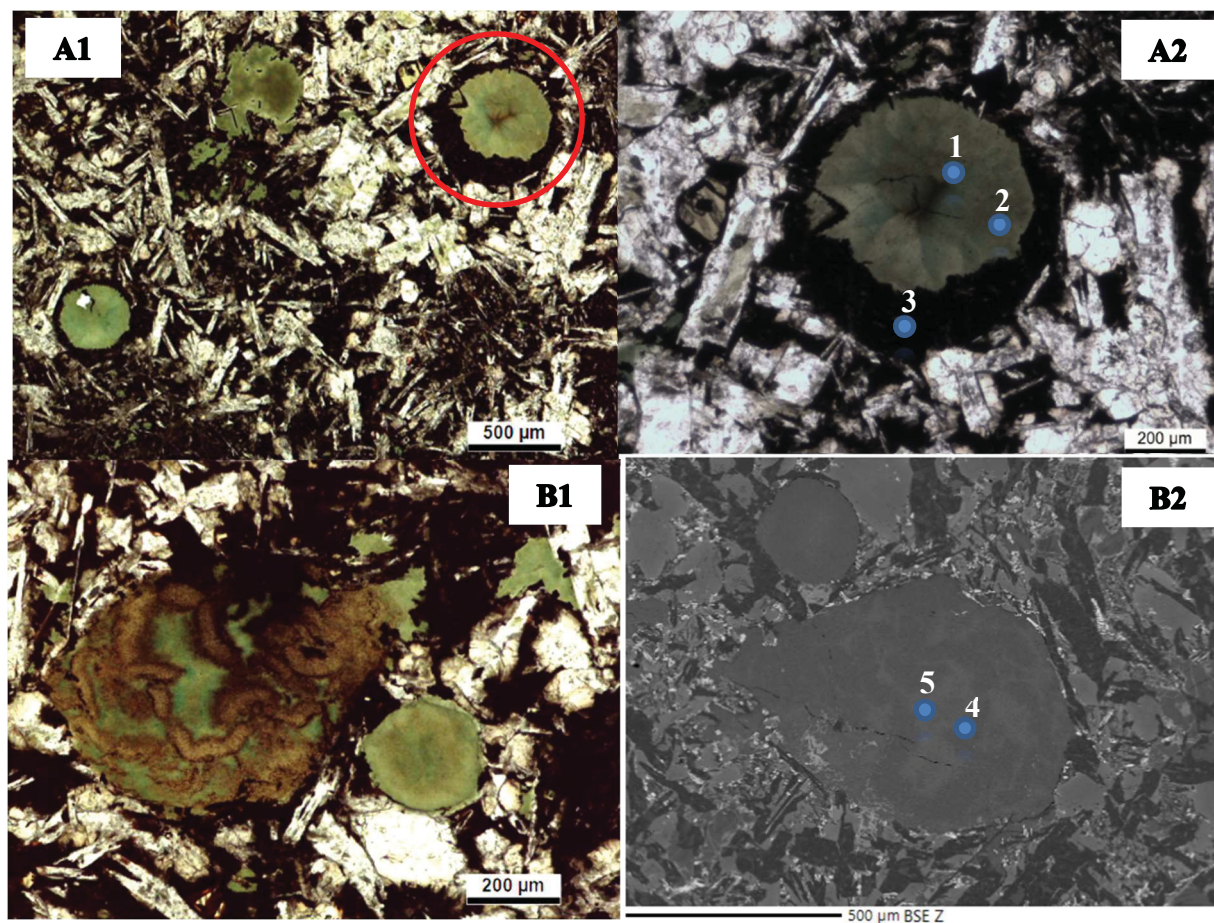


Figure 5.104. Basalt in CAN-F1 (Basalt). Photomicrographs (A1, A2 and B1) in PPL and BSE image (B2), with indication of the points of analysis.

Table 5.35. Sample CAN-F1. EPMA results of volcanic glass (1-2; 4-5) and pyroxene (3).

Oxides (%)	1	2	3	4	5
SiO ₂	54.14	53.18	45.58	53.12	54.62
TiO ₂	0.13	b.d.l.	3.32	0.11	b.d.l.
Al ₂ O ₃	10.45	14.47	4.86	12.00	14.11
FeO	18.08	15.71	19.46	16.89	14.66
MnO	b.d.l.	b.d.l.	0.46	b.d.l.	b.d.l.
MgO	4.08	3.84	9.90	3.86	4.18
CaO	0.26	0.31	16.04	0.28	0.30
Na ₂ O	0.12	0.15	0.33	0.16	0.11
K ₂ O	8.36	8.43	b.d.l.	8.42	8.56
Total	95.64	96.13	99.99	94.84	96.55

b.d.l. = below detection limit

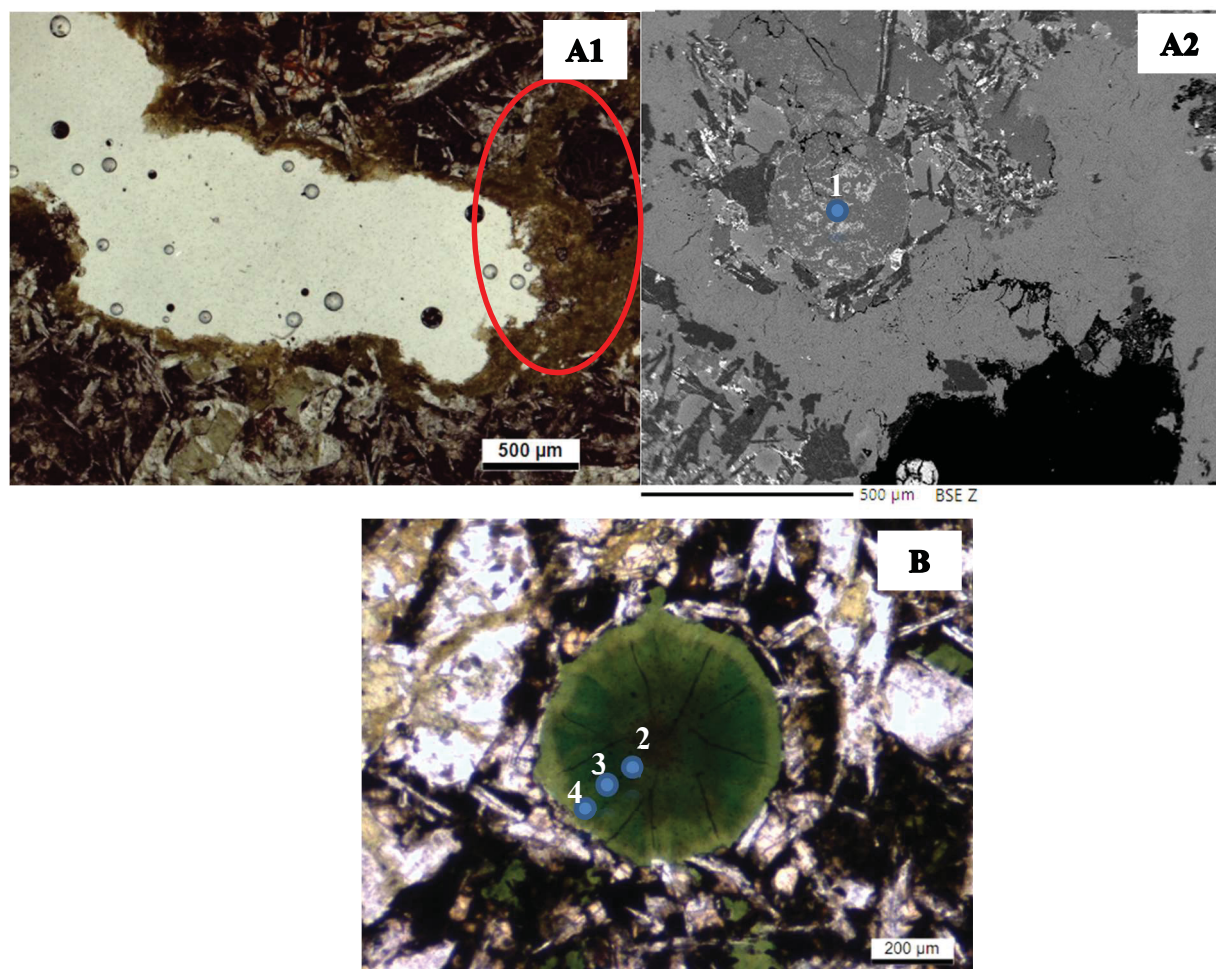


Figure 5.105. Basalt in CAN-F1. Photomicrographs (A1, B) in PPL, BSE image (A2) and respective points of analysis.

Table 5.36. Sample CAN-F1. EPMA results of volcanic glass (1-4).

Oxides (%)	1	2	3	4
SiO ₂	53.88	53.32	53.87	52.48
TiO ₂	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Al ₂ O ₃	13.46	10.09	8.00	14.30
FeO	15.62	17.23	20.01	15.13
MnO	b.d.l.	b.d.l.	0.11	b.d.l.
MgO	3.93	4.80	3.82	3.75
CaO	0.34	0.25	0.21	0.31
Na ₂ O	0.11	b.d.l.	0.17	0.16
K ₂ O	8.35	8.09	8.01	8.40
Total	95.67	93.81	94.26	94.55

b.d.l. = below detection limit

Mozambique

Macroscopically, the MOZ aggregate rock is aphyric, displaying a pinkish-red colour with the majority of the particles exhibiting fine white bands. A part of the aggregate particles shows a whitish to orange tonality in one of the surfaces of the particles. The rock is mainly massive and the particles show angular to subangular shapes, some particles display elongated shape. The aggregate samples were separated by fractions based on texture and colour (Figure 5.106 A and B).

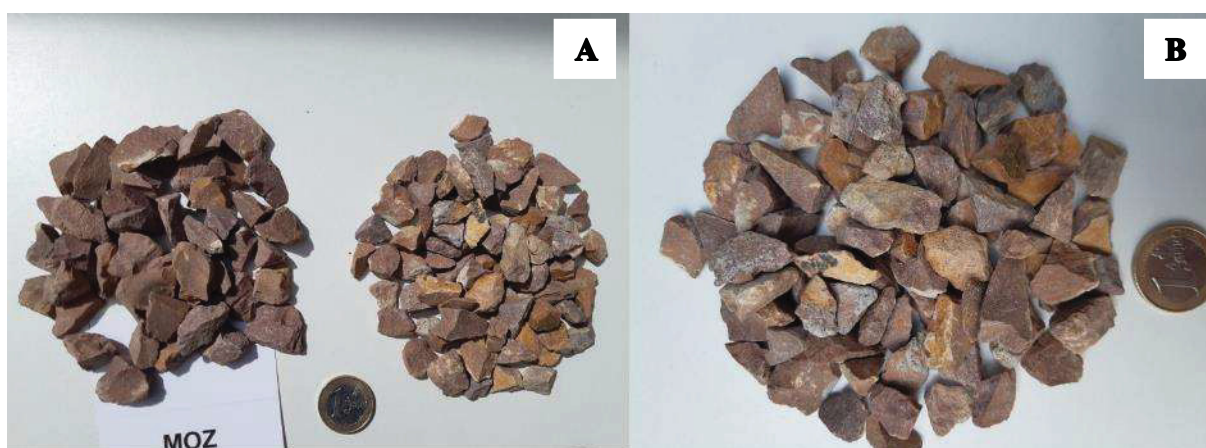


Figure 5.106. Macroscopic photos of the MOZ aggregate with different fractions: A) General view; B) detail of one of the fractions with white and orange surfaces.

In thin section, MOZ sample shows darker and lighter areas. The lighter areas are composed of small grains of quartz, tridymite and possibly feldspars. However, it is difficult to distinguish feldspars without twinning from the silica minerals. The darker areas have a brownish colour and are formed by glass with cryptocrystalline texture (Figure 5.107A and B). Some amphibole, biotite and iron oxides are present.

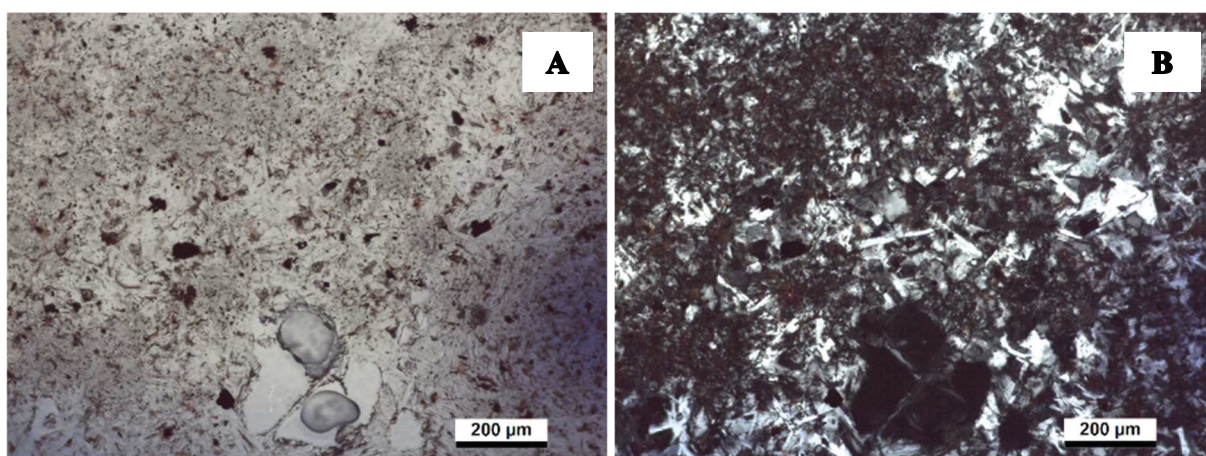


Figure 5.107. Photomicrographs of MOZ rhyolite. B in XPL, A in PPL. A) Brownish area corresponds to volcanic glass; B) Presence of tridymite with a wedge habit.

Some investigation was done by EPMA that revealed that the brownish areas in the photomicrograph (Figure 5.108A1) and the points analysed in Figure 5.108A2 are composed of volcanic glass. The chemical composition is given in Table 5.37.

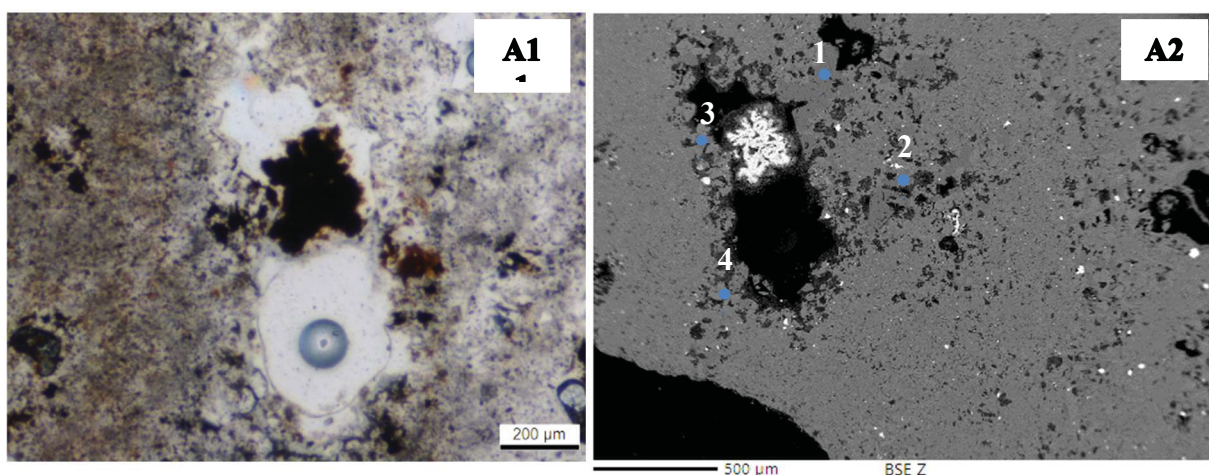


Figure 5.108. Rhyolite in MOZ. Photomicrograph (A1) in PPL, BSE image (A2) and respective points of analysis.

Table 5.37. Sample MOZ. EMPA results of volcanic glass (1-4).

Oxides (%)	1	2	3	4
SiO ₂	68.19	71.04	66.13	64.01
TiO ₂	b.d.l.	0.10	b.d.l.	0.29
Al ₂ O ₃	18.21	15.32	18.85	14.95
FeO	0.26	0.29	0.31	5.69
MnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MgO	b.d.l.	b.d.l.	b.d.l.	0.27
CaO	0.40	0.27	0.45	0.22
Na ₂ O	4.56	1.69	4.52	2.74
K ₂ O	8.17	8.00	8.84	7.88
Total	99.80	97.31	99.12	96.09

b.d.l. = below detection limit

Norway

Macroscopically, NOR aggregate sample is aphanitic displaying a grey colour (Figure 5.109). The particles show angular to subangular forms. The aggregate particles are massive with some dark phenocrysts and others show whitish material filling the vesicles. The aggregate samples were separated by fractions based on texture and colour.



Figure 5.109. Macroscopic photos of the NOR aggregate with different fractions: A) General view; B) detail of one of the fractions with white areas (red arrow).

Under the microscope, NOR sample shows a high degree of alteration. It is composed mainly of phenocrysts of altered plagioclase and amphibole set in a dark groundmass containing opaque minerals, calcite, chlorite, altered plagioclase and brownish material (probably clay minerals). Quartz can also be found in the groundmass.

Plagioclase crystals are being replaced by calcite, chlorite and epidote (Figure 5.110A and B).

Pyroxene is altered to amphibole (Figure 5.110C) with the presence of serpentine and chlorite in some of the phenocrysts.

Calcite exhibits polysynthetic twinning, the chlorites show a yellow green colour with weak birefringence and the epidote crystals are distinguished by the green and yellow colour and display high birefringence colours.

There are also a number of vesicles throughout the rock that are filled with chlorite, calcite, quartz, micro to cryptocrystalline quartz, epidote and serpentine, in some cases (Figure 5.110D, E and F).

Further analysis done by EPMA confirmed the presence of epidote (Figures 5.111A1, A2 and B; Figures 5.112A and B; Tables 5.38 and 5.39) as well as silica minerals (Figures 5.112A and B; Table 5.39) in some of the vesicles.

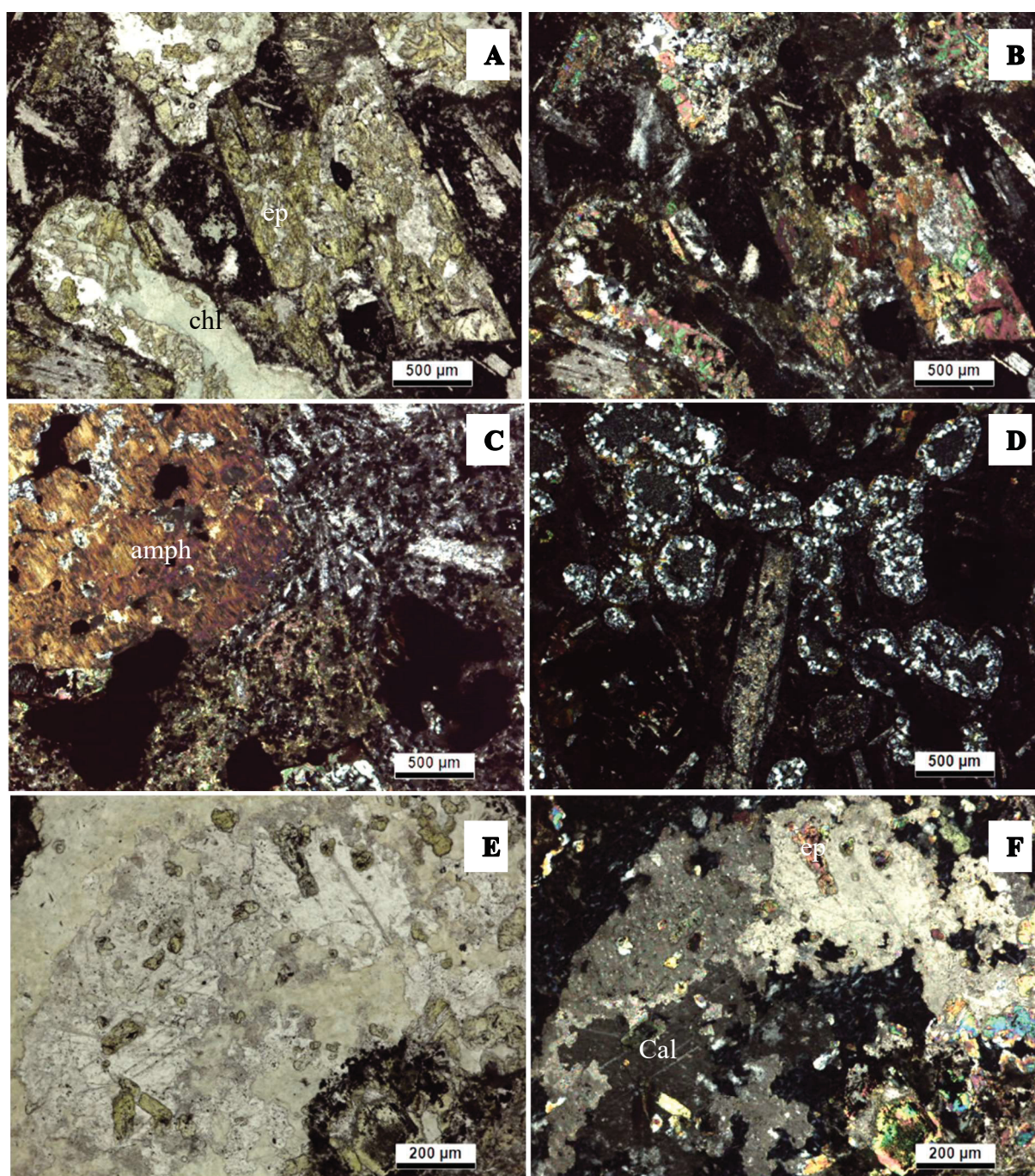


Figure 5.110. Photomicrographs of NOR sample: B, C, D and F in XPL, A and E in PPL. A) and B) Plagioclase with epidotes and chlorite; C) Amphibole after pyroxene; D) Vesicles filled with chlorite and rimmed by cryptocrystalline quartz; E) and F) Vesicles filled with calcite, epidote and chlorite.

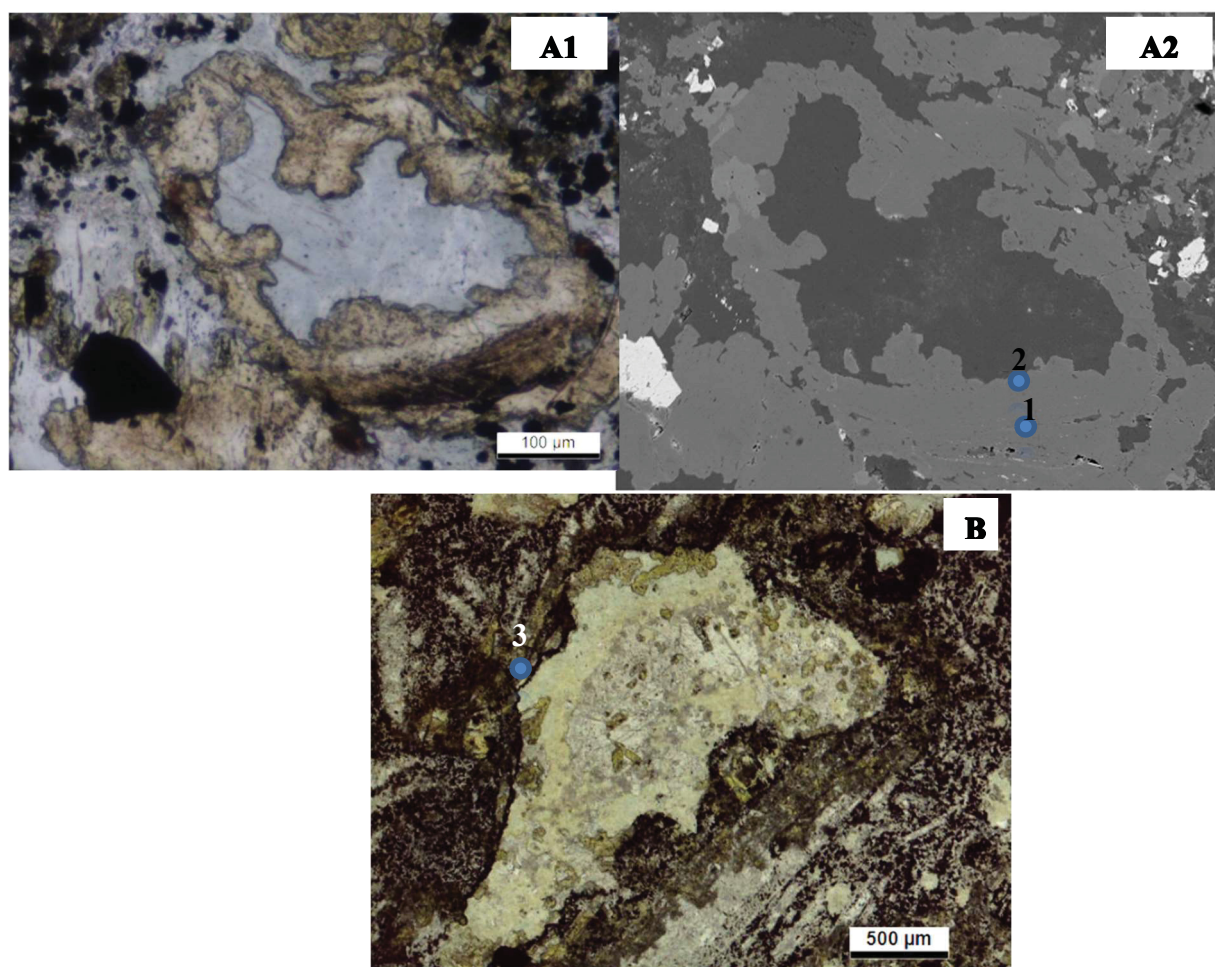


Figure 5.111. Basalt in NOR sample. Photomicrograph (A1, B) in PPL, BSE image (A2) and respective points of analysis.

Table 5.38. Sample NOR. EMPA results of epidote (1-3).

Oxides (%)	1	2	3
SiO ₂	37.27	37.39	37.18
TiO ₂	0.15	b.d.l.	b.d.l.
Al ₂ O ₃	21.68	21.91	19.89
FeO	14.34	13.86	16.39
MnO	0.27	0.35	0.17
MgO	0.12	0.10	b.d.l.
CaO	22.81	22.90	22.98
Na ₂ O	b.d.l.	b.d.l.	b.d.l.
K ₂ O	b.d.l.	b.d.l.	b.d.l.
Total	96.65	96.53	96.62

b.d.l. = below detection limit

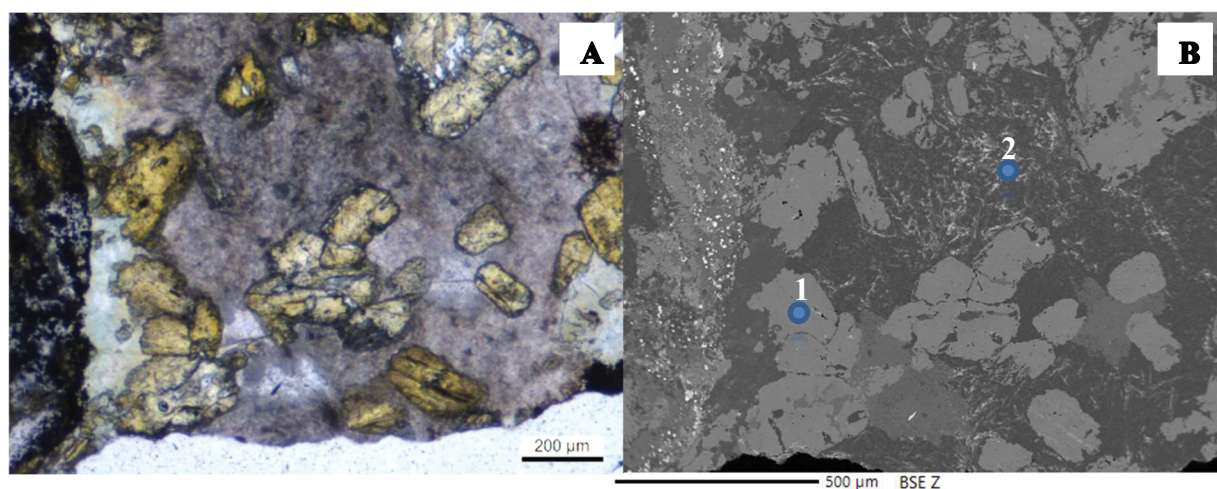


Figure 5.112. Basalt in NOR sample. Photomicrograph (A) in PPL, BSE image (B) and respective points of analysis.

Table 5.39. Sample NOR. EMPA results of epidote (1) and silica minerals (2).

Oxides (%)	1	2
SiO ₂	37.02	97.77
TiO ₂	0.17	b.d.l.
Al ₂ O ₃	20.34	0.47
FeO	15.96	0.47
MnO	0.21	b.d.l.
MgO	b.d.l.	0.69
CaO	22.89	0.34
Na ₂ O	b.d.l.	b.d.l.
K ₂ O	b.d.l.	b.d.l.
Total	96.59	99.76
b.d.l. = below detection limit		

Turkey

Macroscopically, the rock sample from Turkey is aphanitic, mainly with a grey colour; however, some aggregate particles show a greenish tone (Figure 5.113). Half of the aggregate particles show a beige or red colour material on one of the surfaces, and seem to be punctuated by white minerals. Elongated vitreous crystals are visible in different particles. The samples are massive in texture with angular to subangular forms. The aggregate samples were separated by fractions based on texture and colour.



Figure 5.113. Macroscopic photos of the TK aggregate with different fractions: A) General view; B) detail of one of the fractions with white dots and the surfaces lined by a beige or red colour material.

In thin section, the andesitic sample is porphyritic in texture with phenocrysts, mainly of plagioclase, clinopyroxene (pigeonite-augite) and orthopyroxene (hypersthene), set in a fine glassy groundmass.

The plagioclase occurs in euhedral to subhedral crystals displaying concentric compositional zoning. They form sometimes glomeroporphyritic clusters either alone or together with pyroxenes. Volcanic glass inclusions are frequent and there is some degree of alteration along the cracks and cleavages (Figure 5.114A).

Some reaction rims are visible in some plagioclase crystals. Plagioclase and pyroxene occur mainly in subhedral crystals. Augite sometimes appears twinned and in euhedral crystals. Olivine is, in some particles, highly altered into a red brown material that looks like iddingsite, maintaining the euhedral habit (Figure 5.114B). Carbonates are scattered irregularly throughout the rock forming pseudomorphs (Figure 5.114C) or, less commonly, filling vesicles (Figure 5.114D).

Opaque minerals are accessory minerals and occur associated with pyroxene or dispersed throughout the rock. Small number of xenoliths are present in this rock containing plagioclase and clinopyroxenes phenocrysts together with opaque minerals (Figure 5.114E).

The groundmass is hyalopilitic with a brownish colour, isotropic in XPL, and it contains microlites of plagioclase, augite and hypersthene (Figure 5.114F).

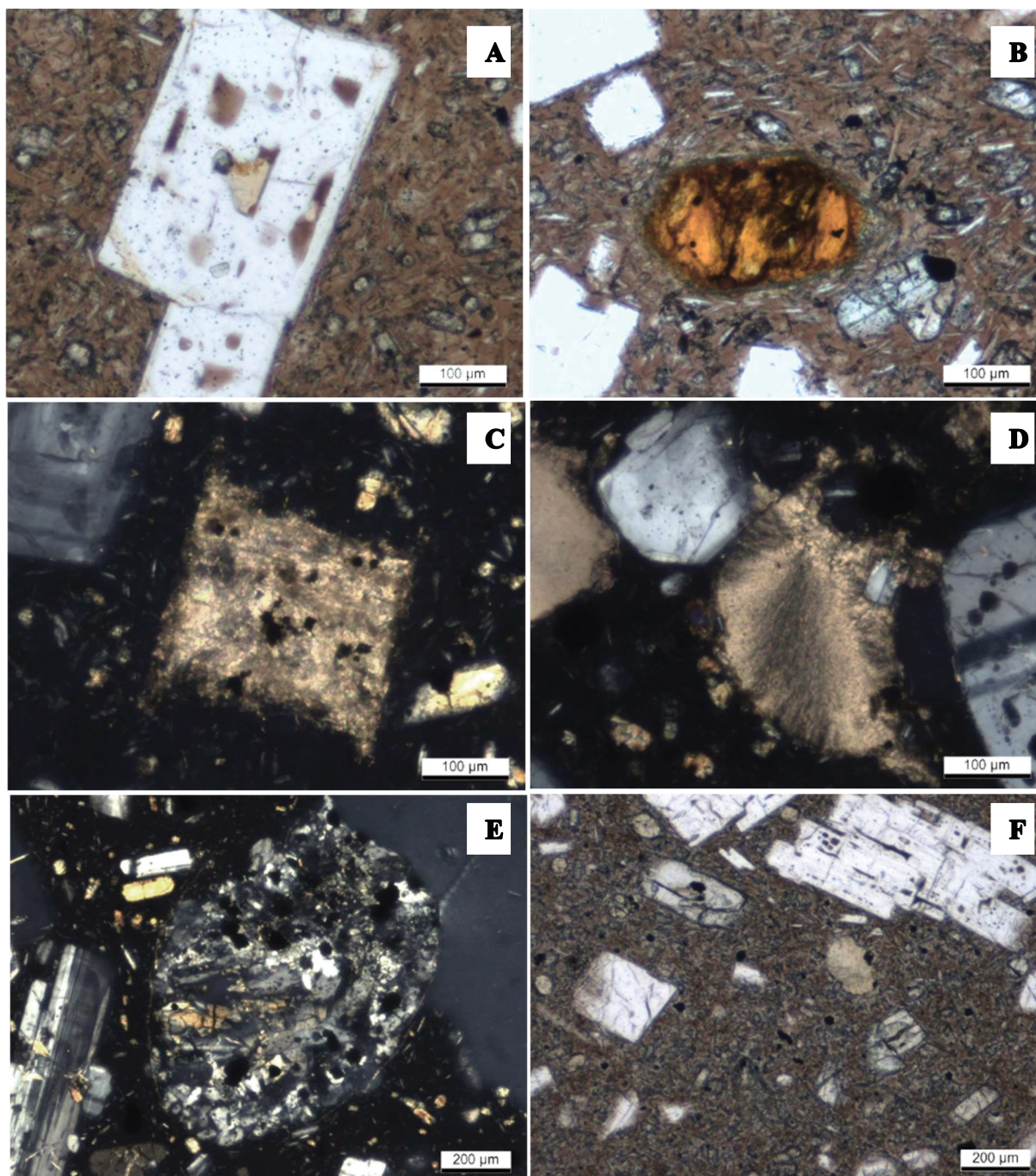


Figure 5.114. Photomicrographs of the Turkey sample: C, D and E in XPL, A, B and F in PPL. A) Plagioclase phenocryst with glass inclusions; B) Olivine crystals completely replaced by iddingsite; C) Calcite pseudomorph; D) Calcite filling a vesicle; E) Xenolith containing plagioclase, clinopyroxene and opaque minerals; F) Groundmass containing abundant brown volcanic glass.

EDS analysis was used to identify an isotropic yellowish material filling a crack (Figures 5.115A and B). EPMA were used to identify some of the components. Volcanic glass inclusions in plagioclase phenocrysts contain more than 70% in SiO_2 (Figures 5.116 and 5.117; Table

5.40 and 5.41). The volcanic glass in the groundmass was also analysed by EPMA containing more than 70% of SiO_2 (Figures 5.117 and 5.118; Tables 5.41 and 5.42).

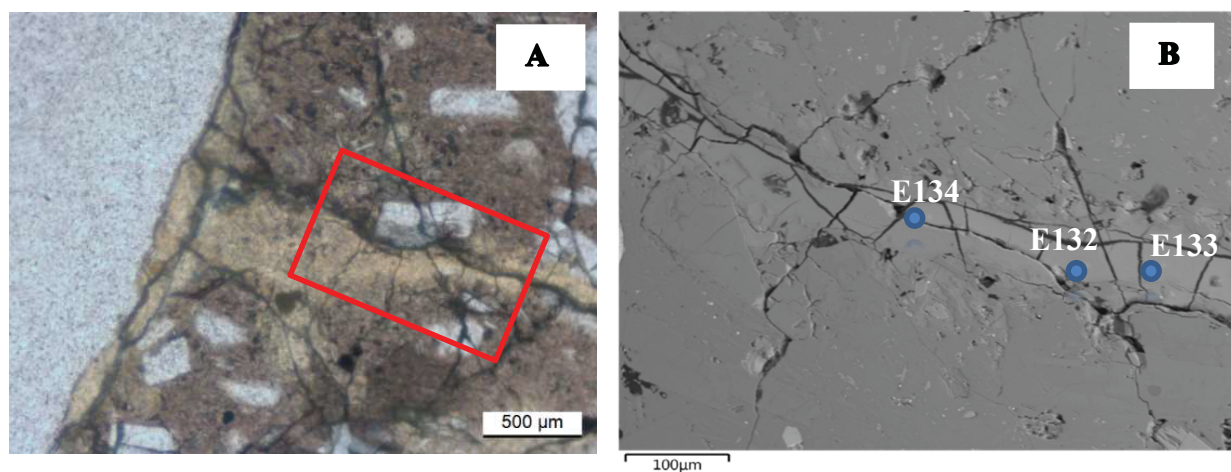


Figure 5.115A. TK andesite. Photomicrograph (A) in PPL and BSE image (B) with locations of the EDS spectra of volcanic glass (E132-E134).

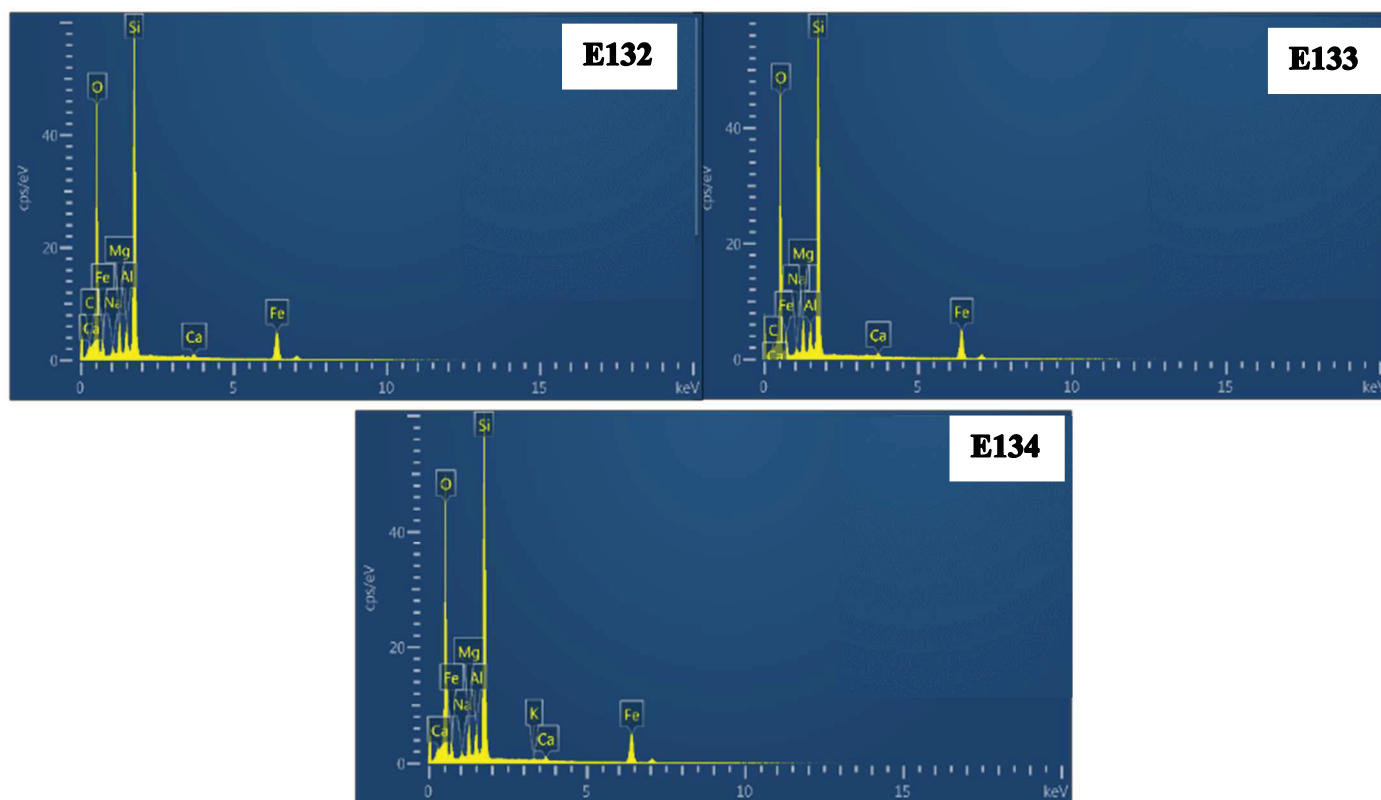


Figure 5.115B. TK andesite: EDS spectra of volcanic glass (E132-E134).

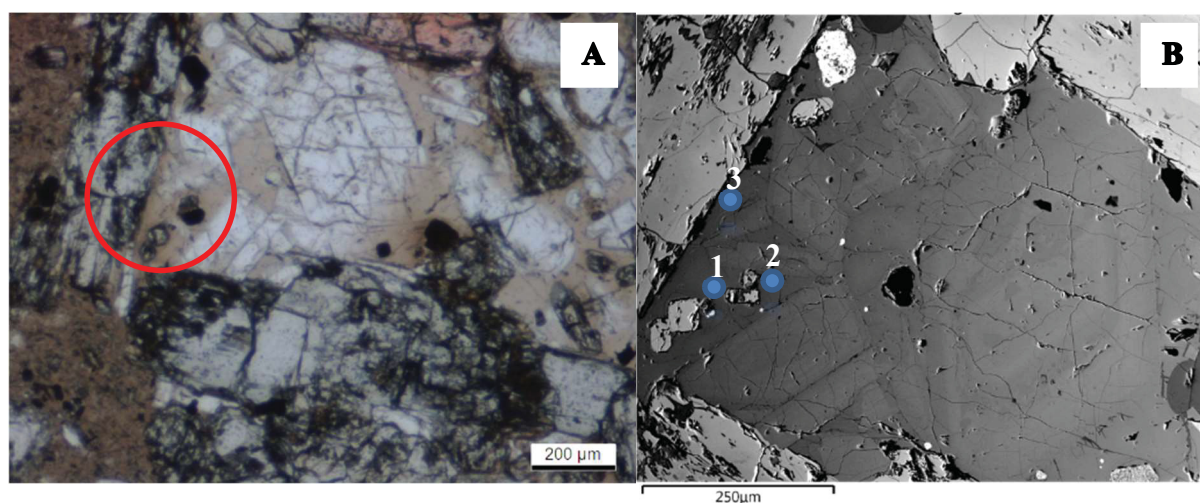


Figure 5.116. TK andesite. Photomicrograph (A) in PPL and BSE image (B) and respective points of analysis.

Table 5.40. Sample TK. EPMA results of inclusions of volcanic glass (1-3) from Figure 5.116.

Oxides (%)	1	2	3
SiO ₂	72.30	72.49	72.47
TiO ₂	0.43	0.43	0.34
Al ₂ O ₃	11.89	12.01	12.36
FeO	2.67	2.53	2.65
MnO	b.d.l.	b.d.l.	b.d.l.
MgO	0.40	0.38	0.37
CaO	1.20	1.23	1.15
Na ₂ O	0.45	0.29	0.37
K ₂ O	3.22	3.22	3.25
Total	92.93	92.92	93.34

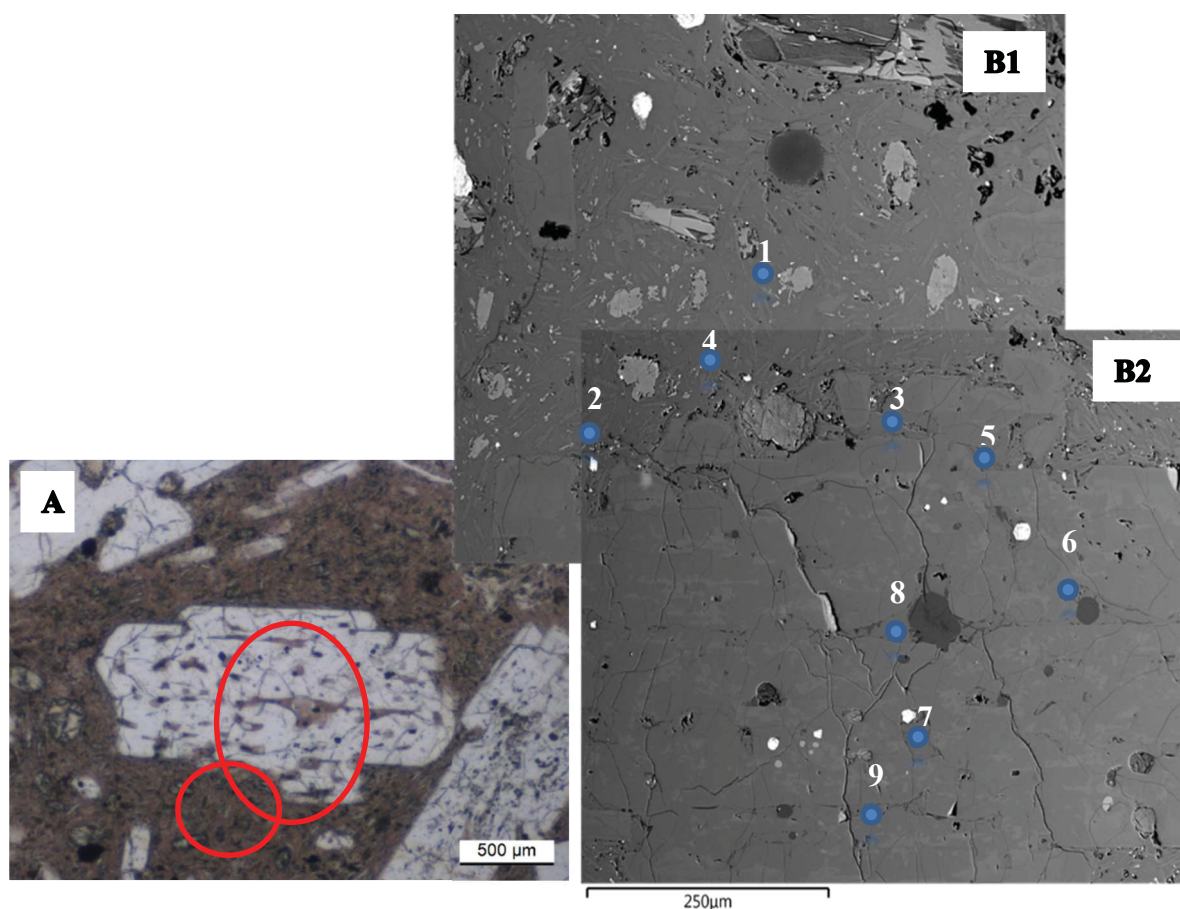


Figure 5.117. TK andesite. Photomicrograph (A) in PPL and BSE images (B1 and B2) and respective points of analysis.

Table 5.41. Sample TK. EPMA results of volcanic glass: groundmass (1, 2, 4) and inclusions in the plagioclase (3, 5-9) from Figure 5.117.

Oxides (%)	1	2	3	4	5	6	7	8	9
SiO ₂	72.94	71.21	71.57	71.22	73.11	70.87	71.19	70.97	70.53
TiO ₂	0.75	0.77	0.70	0.75	0.77	0.70	0.71	0.71	0.74
Al ₂ O ₃	12.43	12.17	12.09	12.32	12.48	12.08	11.98	11.95	11.75
FeO	2.53	2.41	2.44	2.32	2.51	2.97	2.60	2.89	3.01
MnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MgO	0.32	0.26	0.26	0.24	0.35	0.45	0.41	0.38	0.40
CaO	0.98	0.93	0.94	1.11	0.88	1.01	0.94	1.01	1.03
Na ₂ O	0.26	0.48	0.49	0.63	0.23	0.49	0.41	0.59	0.63
K ₂ O	2.66	4.97	4.72	4.38	2.60	4.51	4.44	4.79	4.83
Total	93.35	93.67	93.69	93.40	93.50	93.57	93.15	93.67	93.47

b.d.l. = below detection limit

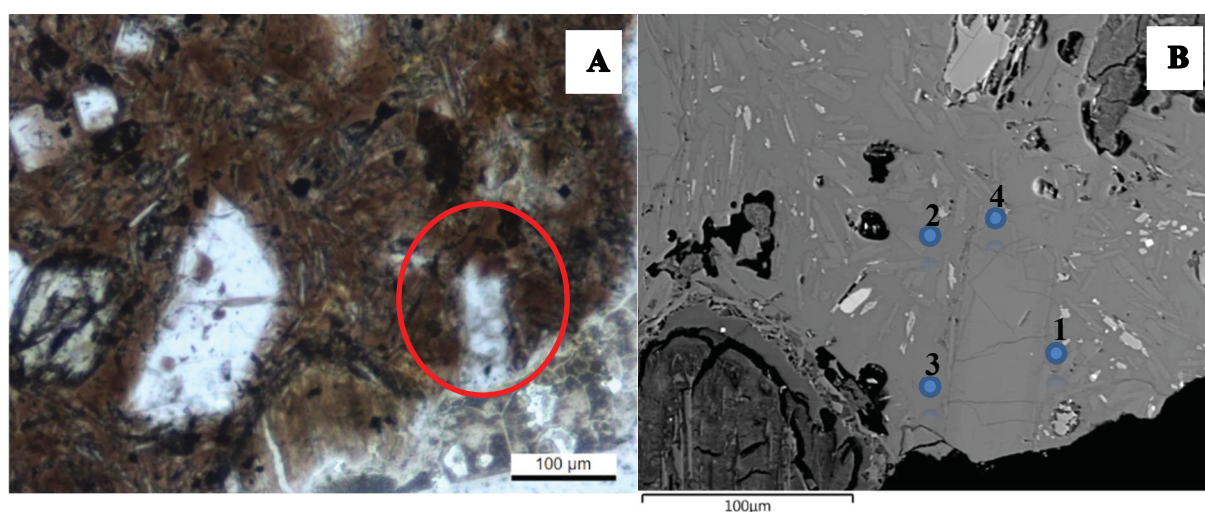


Figure 5.118. TK andesite. Photomicrograph (A) in PPL and BSE image (B) showing the points of analysis.

Table 5.42. Sample TK. EMPA results of volcanic glass (1-4) from Figure 5.118.

Oxides (%)	1	2	3	4
SiO ₂	73.15	72.39	71.58	71.76
TiO ₂	0.90	0.95	0.90	0.90
Al ₂ O ₃	12.58	11.73	12.17	11.70
FeO	2.50	2.52	1.99	2.47
MnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.
MgO	0.22	0.21	0.14	0.21
CaO	0.91	0.82	0.69	0.80
Na ₂ O	0.25	0.49	0.47	0.40
K ₂ O	2.44	4.58	5.14	4.31
Total	93.52	93.56	93.59	93.02

b.d.l. = below detection limit

5.2.2. Mortar studies

5.2.2.1. Expansion tests - Accelerated mortar-bar test at 80°C (CSA A23.2-25A/ASTM C 1260)

A number of accelerated mortar bar tests were performed as part of the present study. From the thirty mixes prepared at Université Laval, in Québec, Canada, six mixes were manufactured with aggregates from Continental regions (BRAZ, CAN, MOZ, NOR and TK). Spratt and GBS sand were used as reference in each graph. The characteristics of the mortars are the same as the ones presented in Table 4.13 in Chapter 4. The AMBT method is described by the CSA A23.2-25A (2019), ASTM C 1260 and RILEM AAR-2 (2016) but the limits are

provided by the CSA Standard Practice A23.2-27A (2019), ASTM C 1778 (2020) and RILEM AAR-0 (2016).

Brazil

The results of the AMBT for the Brazilian aggregate show that the 14-day expansion is 0.48% and continues to increase until the end testing, reaching an expansion 0.55% at 28 days. But after the 14 days, the expansion started to level off (Figure 5.119).

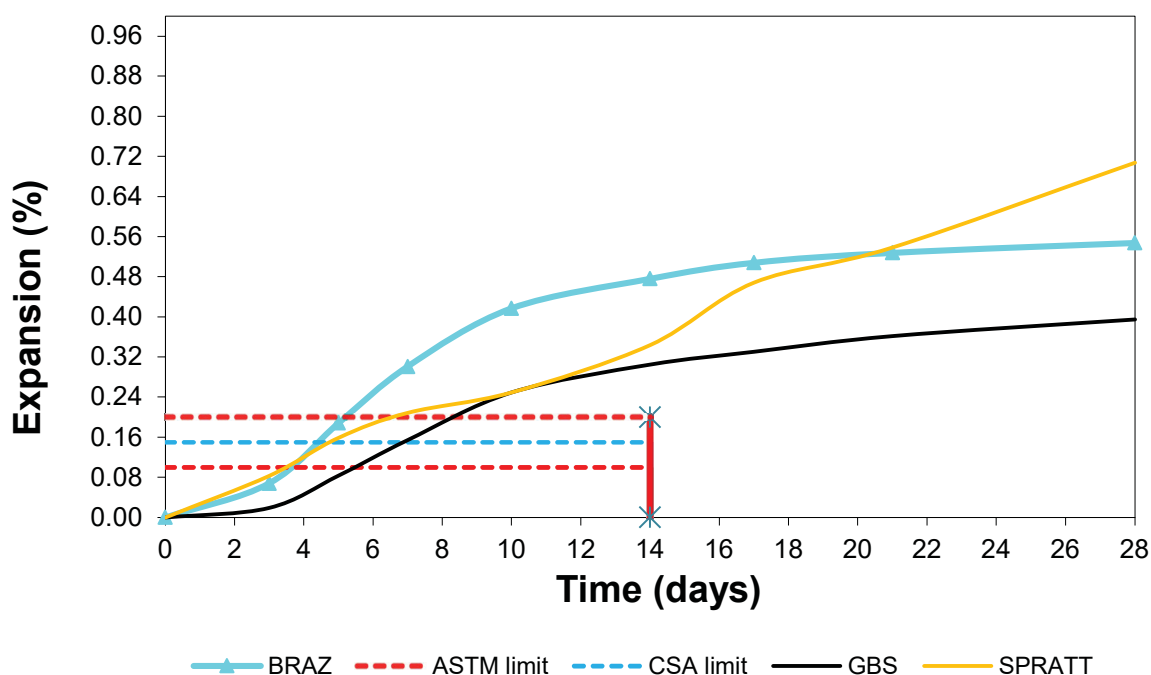


Figure 5.119. Expansion results of the AMBT (CSA A23.2-25A) concerning the BRAZ aggregate.

According to ASTM C 1778 (2020) standard and recommendation RILEM AAR-0 (2016), this aggregate is considered potentially reactive and according to the CSA A23.2-27A (2019), it is classified as extremely reactive.

Canada

The mortar bars manufactured with aggregate CAN present very low expansion, i.e. 0.02% at 14 days and 0.03% at the end of 28 days of testing.

According to all standards (ASTM C 1778; CSA 23.2-27A) and recommendations (RILEM AAR-0, 2016), CAN aggregate is considered non-reactive.

The results for the accelerated mortar-bar method for the Canadian aggregate CAN are shown in Figure 5.120.

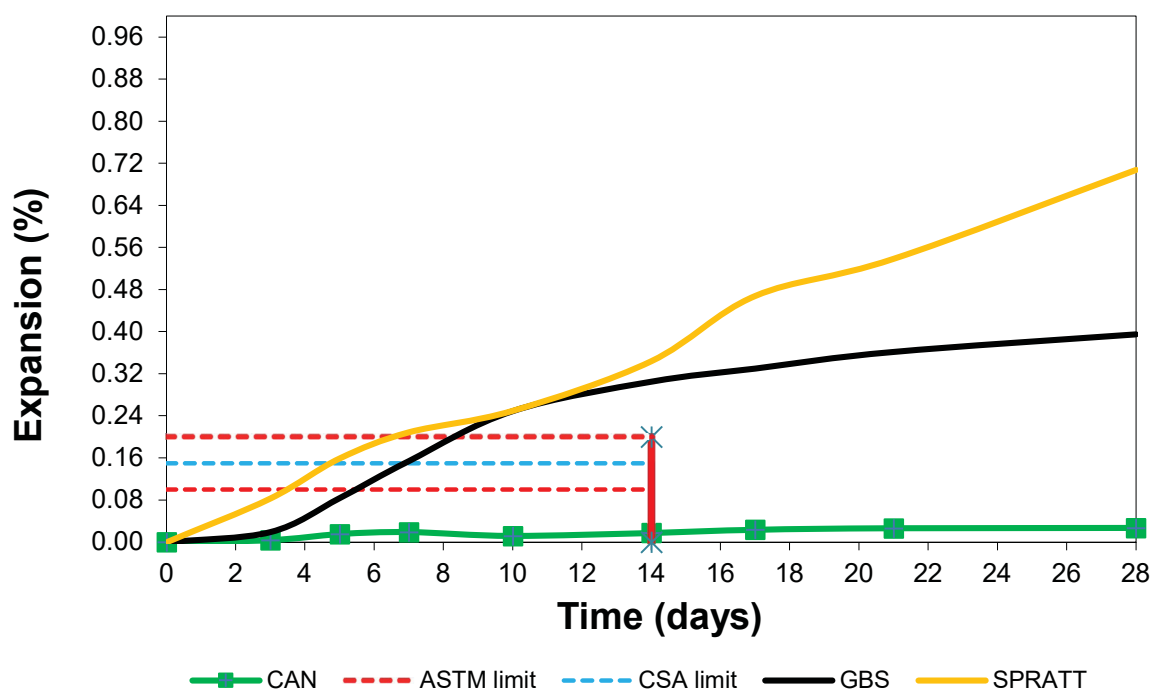


Figure 5.120. Expansion results of the AMBT (CSA A23.2-25A) concerning the CAN aggregate.

Mozambique

The mortar bars incorporating MOZ aggregate present some expansion. At 14 days, MOZ showed expansion values of 0.22%, which reached 0.36% at the end of 28 days of testing. There is a slight tendency for stabilization with time, mainly after 18 days of testing.

According to ASTM C 1778 (2020) standard and recommendation RILEM AAR-0 (2016), this aggregate is considered potentially reactive; it is highly reactive according to CSA Standard Practice A23.2-27A (2019).

The results for the accelerated mortar-bar method of the Mozambique aggregate are shown in Figure 5.121.

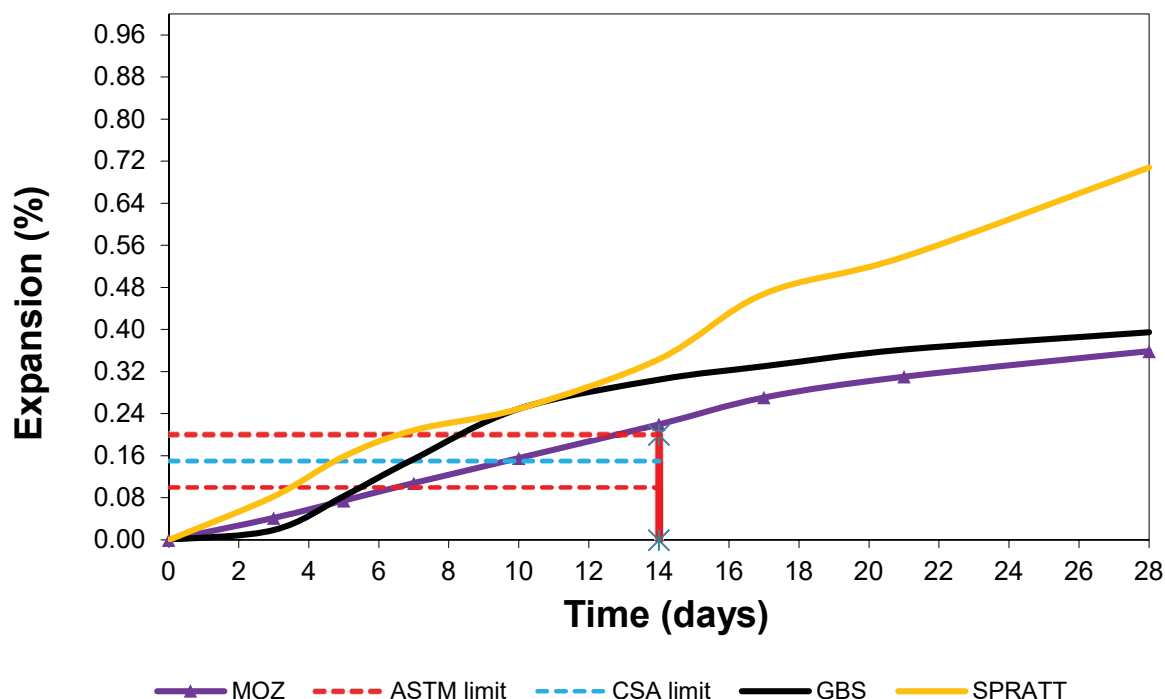


Figure 5.121. Expansion results of the AMBT (CSA A23.2-25A) concerning the MOZ aggregate.

Norway

The mortar bars made with NOR aggregate show low expansion. At 14 days, the expansion is of 0.07% and it reaches 0.17% at the end of 28 days of testing.

The main increase in the rate of expansion occurs between day 10 and 21, constant expansive rate until the end of the test period. Although the value is near the limit, all standards (ASTM C 1778, 2020; CSA A23.2-27A, 2019) and recommendations (RILEM AAR-0, 2016), consider this aggregate as non-reactive.

The results for the accelerated mortar bar test with the NOR aggregate are shown in Figure 5.122.

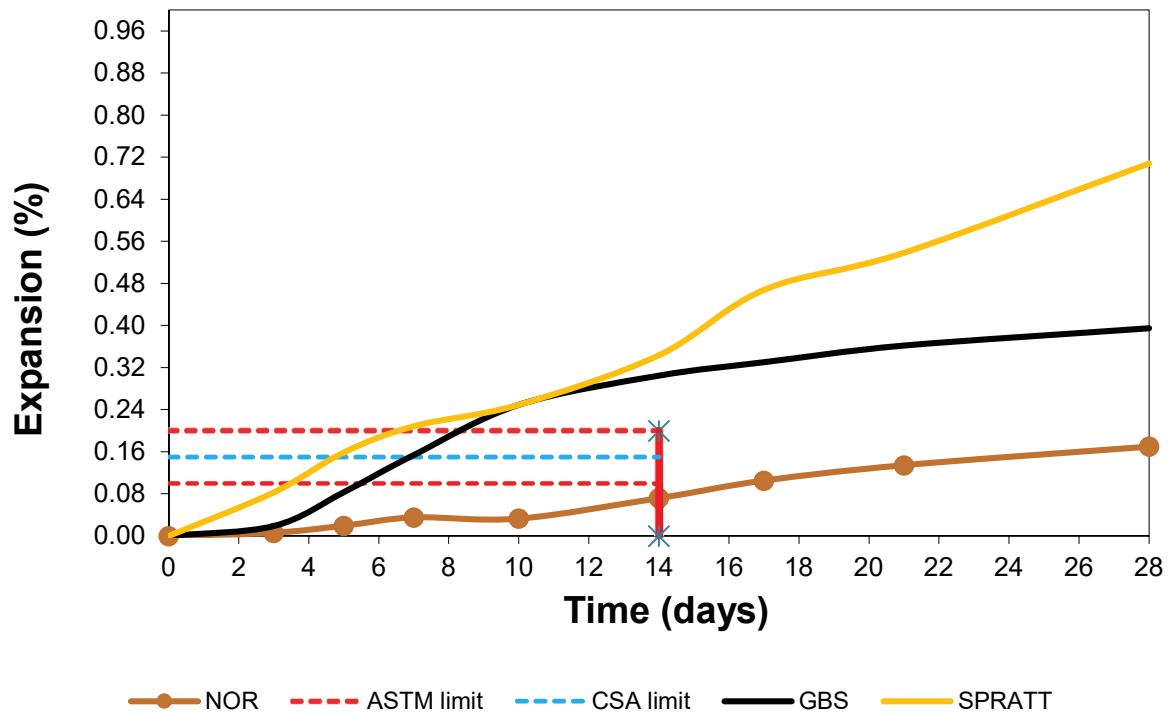


Figure 5.122. Expansion results of the AMBT (CSA A23.2-25A) concerning the NOR aggregate.

Turkey

The results of the AMBT for the TK aggregate show that at 14 days, the expansion value is 0.98% and continues to increase even at 28 days of testing, where it reaches an expansion of 1.62%. At the end of testing, the TK aggregate does not show any signs of stabilization.

According to the ASTM C 1778 (2020) standard and recommendation RILEM AAR-0 (2016), this aggregate is considered potentially reactive and according to Standard Practice CSA A23.2-27A (2019), it is classified as extremely reactive.

The results for the accelerated mortar-bar method for the TK aggregate are shown in Figure 5.123.

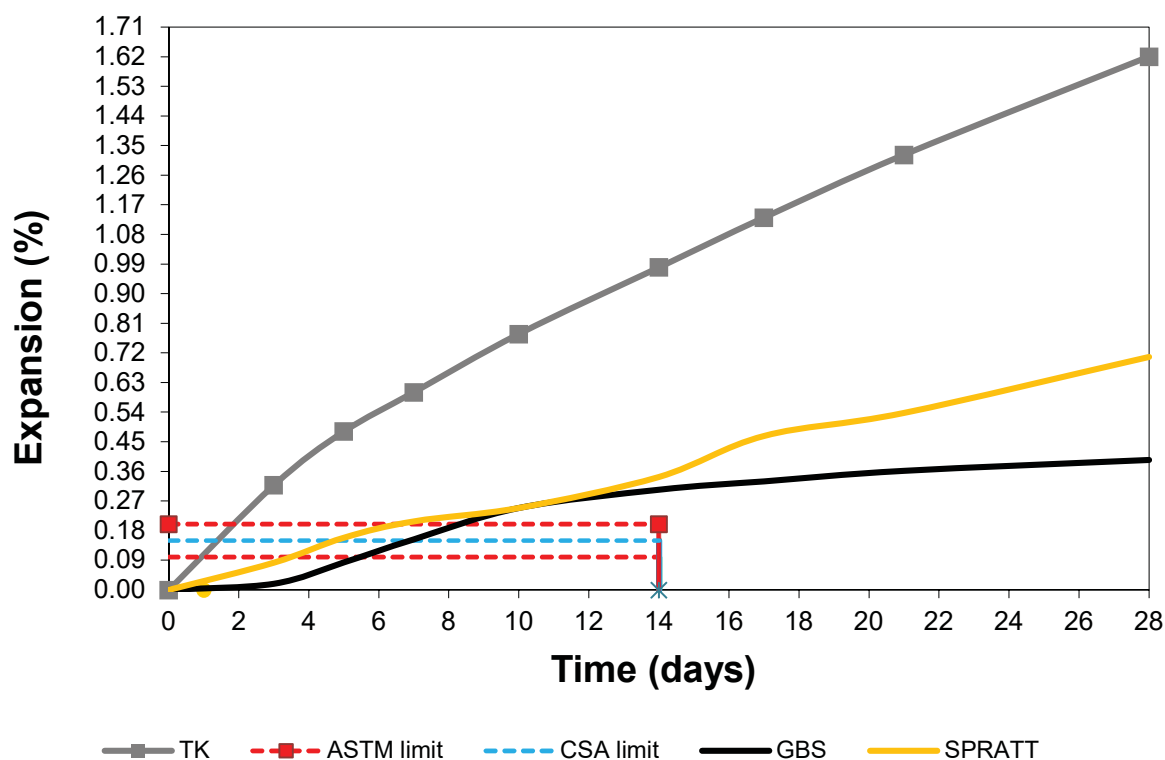


Figure 5.123. Expansion results of the AMBT (CSA A23.2-25A) of the TK aggregate.

5.2.2.2. Post-mortem mortar petrography

Brazil

The mortar bars from BRAZ were manufactured with basaltic crushed rocks. The texture and mineralogy of the aggregate particles are the same as described in section 5.2.2.

In general, there are several thin cracks in the cement matrix, part of them with isotropic brownish gel. There are a number of aggregate particles with cracks containing gel that extend into the cement paste (Figure 5.124A and B); in other cases, the cracks with gel are limited to the aggregate particles (Figure 5.124C and D). The cracks with gel frequently connect aggregate particles by crossing or outlining them and sometimes connect with pores.

Most of the voids are completely filled with gel (Figure 5.124E); others are just lined by gel together with acicular crystals of ettringite (Figure 5.124F).

There are evidences for an ongoing ASR that involves some of the basaltic particles in the mortar bar.

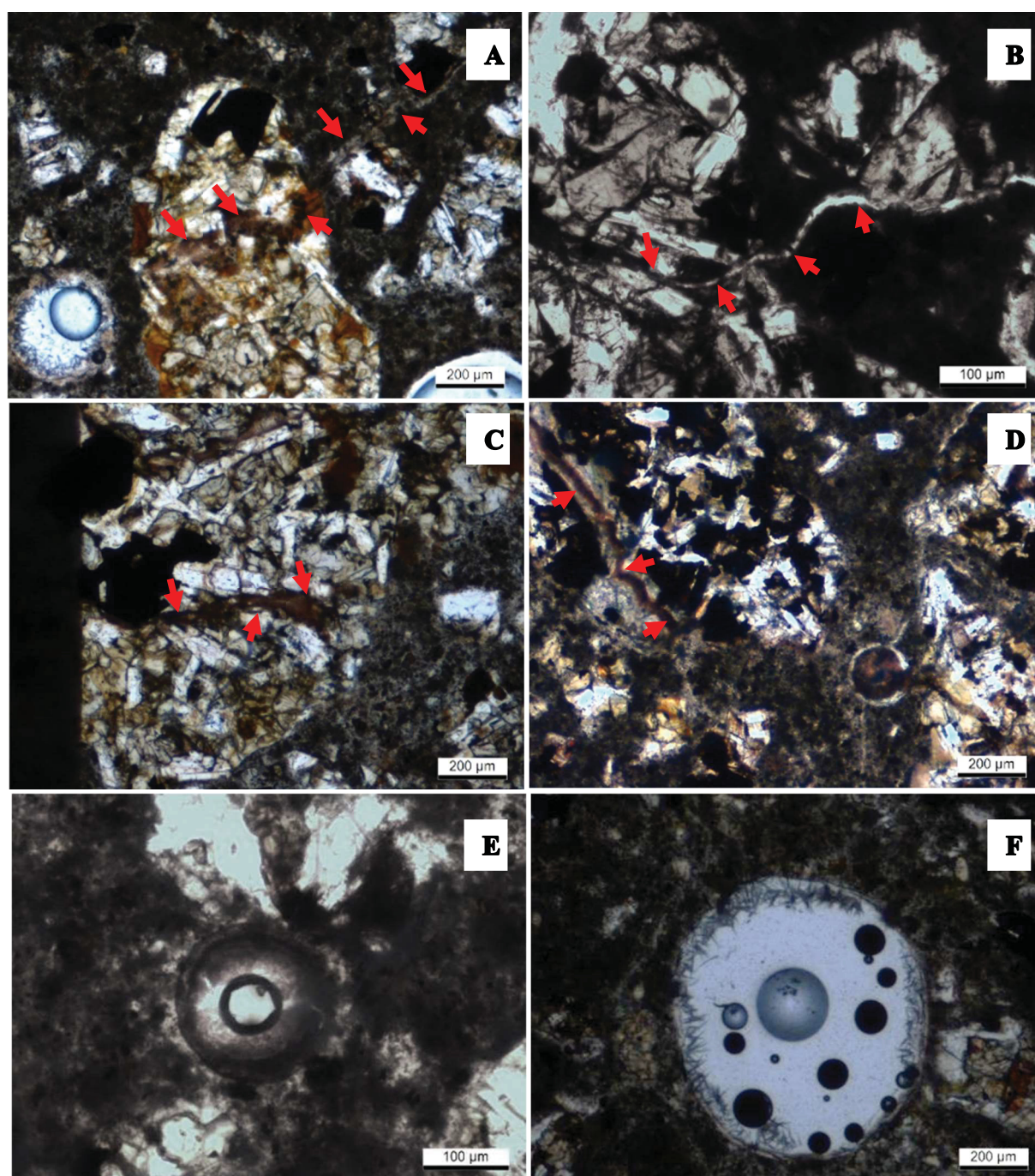


Figure 5.124. Photomicrographs of BRAZ mortar bar. All photos in PPL. A) Crack with brownish gel within a basaltic aggregate particle that extends to the cement paste; B) Crack with brownish gel within another basaltic aggregate particle that extends into the cement paste; C) Crack with volcanic glass inside the aggregate particle; D) Crack with gel limited to another aggregate particle and a void also containing gel; E) Void partially filled with brownish gel; F) Pore lined by ettringite crystals.

Canada

In the mortar bar containing the CAN basaltic crushed rocks, the texture and mineralogy of the aggregate particles are the same as described in section 5.2.2. However, there are some aggregate particles formed just by calcite or plagioclase and some particles show darker colours than the ones identified in the thin sections of the aggregate.

In general, there are very few cracks in the cement paste (Figure 5.125A). Some aggregate particles are cracked but the cracks are empty or filled with calcite (e.g. veins) and do not extend into the cement paste (Figure 5.125B).

The voids are usually empty, but some appear lined or completely filled with a brown material that could be polishing material (Figure 5.125C).

There is no evidence for an ongoing ASR in the CAN mortar.

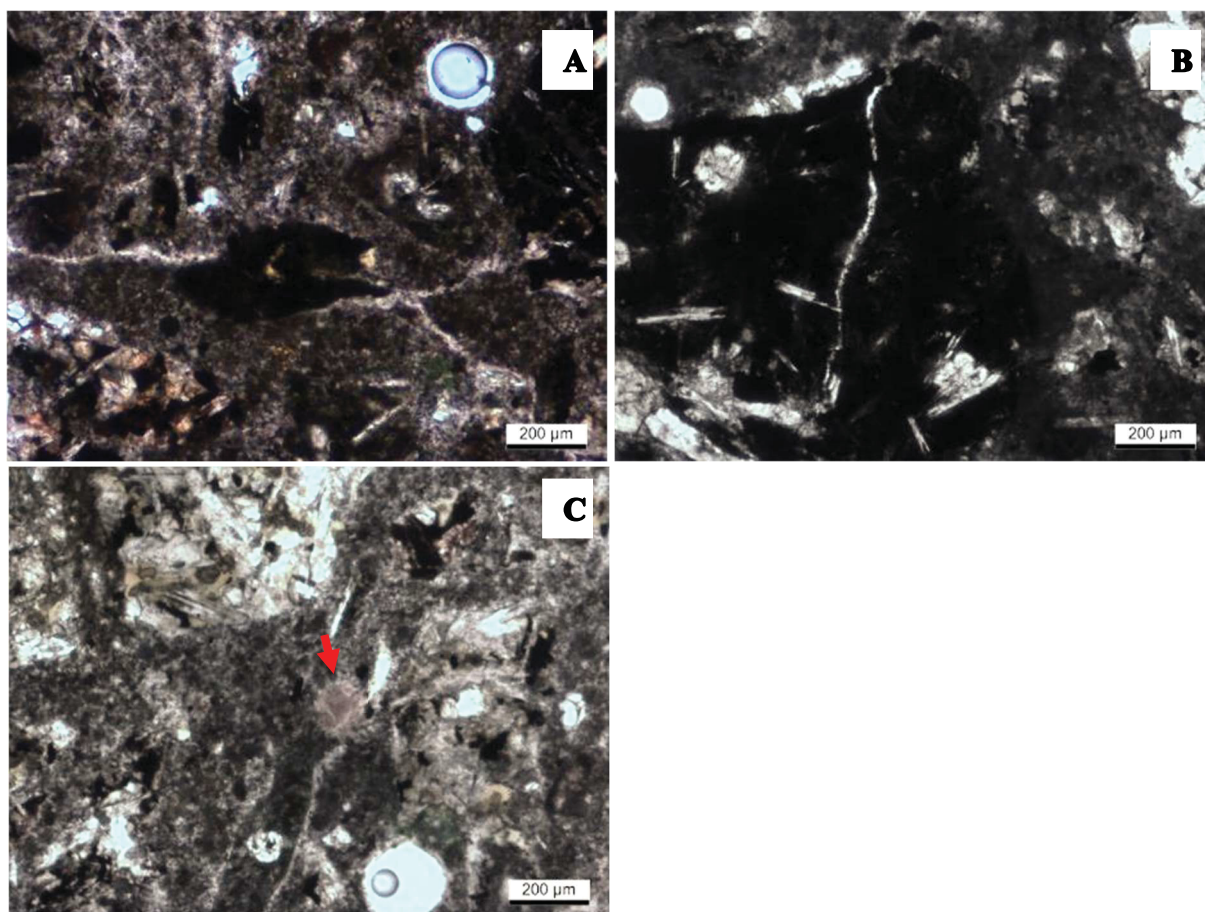


Figure 5.125. Photomicrographs of CAN mortar bar. All photos in PPL. A) Cracks in the cement paste; B) Crack within a basaltic aggregate particle, empty and extending into the cement paste; C) Cracks and a void filled with brownish material (red arrow).

The Spratt mortar bar, used as reference in the laboratory tests, contains crushed siliceous limestone aggregate. The various aggregate particles show different features. Some

aggregate particles contain carbonate and siliceous bioclasts, while others are mainly composed of calcite and others contain a reddish brown material (probably clay minerals and limonite). The mortar bars petrographic analysis shows that there are several cracks in the aggregate particles, some being quite large (Figure 5.126A). These cracks extend into the cement paste and connect to other aggregate particles, some of them being partly filled with gel (Figure 5.126B). Some of the voids are filled or partly filled by a brownish material that could be secondary products.

There is evidence for an ongoing ASR in the Spratt mortar.

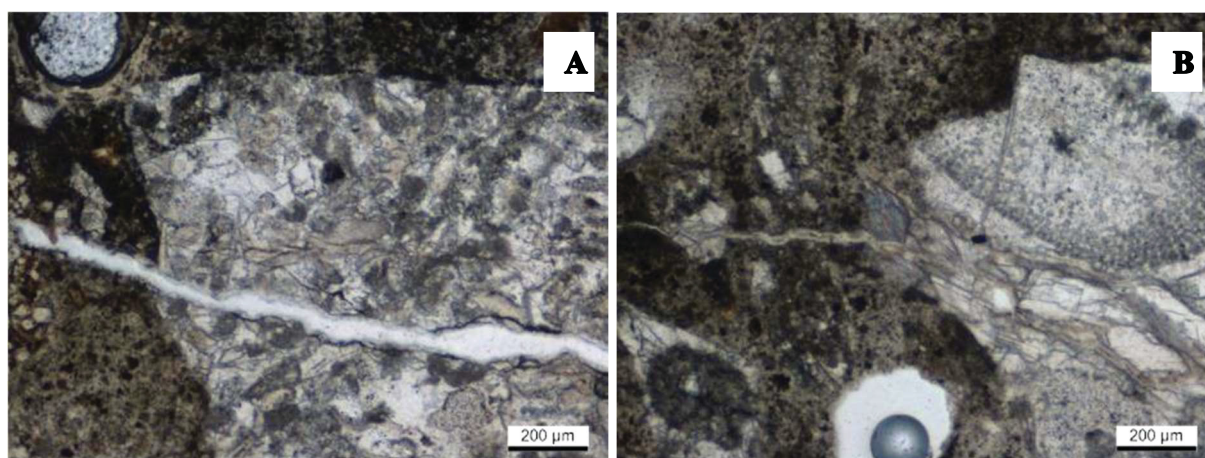


Figure 5.126. Photomicrographs of Spratt (siliceous limestone) mortar bar, used as reference in the laboratory tests. All photos in PPL. A) Crack crossing an aggregate particle and extending into the cement paste, lined by gel; B) Crack with gel crossing the cement paste and an aggregate particle.

Mozambique

The texture and mineralogy of the rhyolitic aggregate used in the manufacture of the mortar bars are the same as described in section 5.22.

The MOZ mortar shows several minor cracks in the cement paste (Figure 5.127A) and also some wide and long cracks filled with brownish gel. These cracks begin inside the rhyolite particles and extend into the cement paste crossing several other particles (Figure 5.127B, C and D). Sometimes, they connect with voids (Figure 5.127E). The majority of the voids are partly filled or lined by brownish gel (Figure 5.127F).

There is a strong evidence for an ongoing ASR that involves the rhyolite aggregate particles in the mortar.

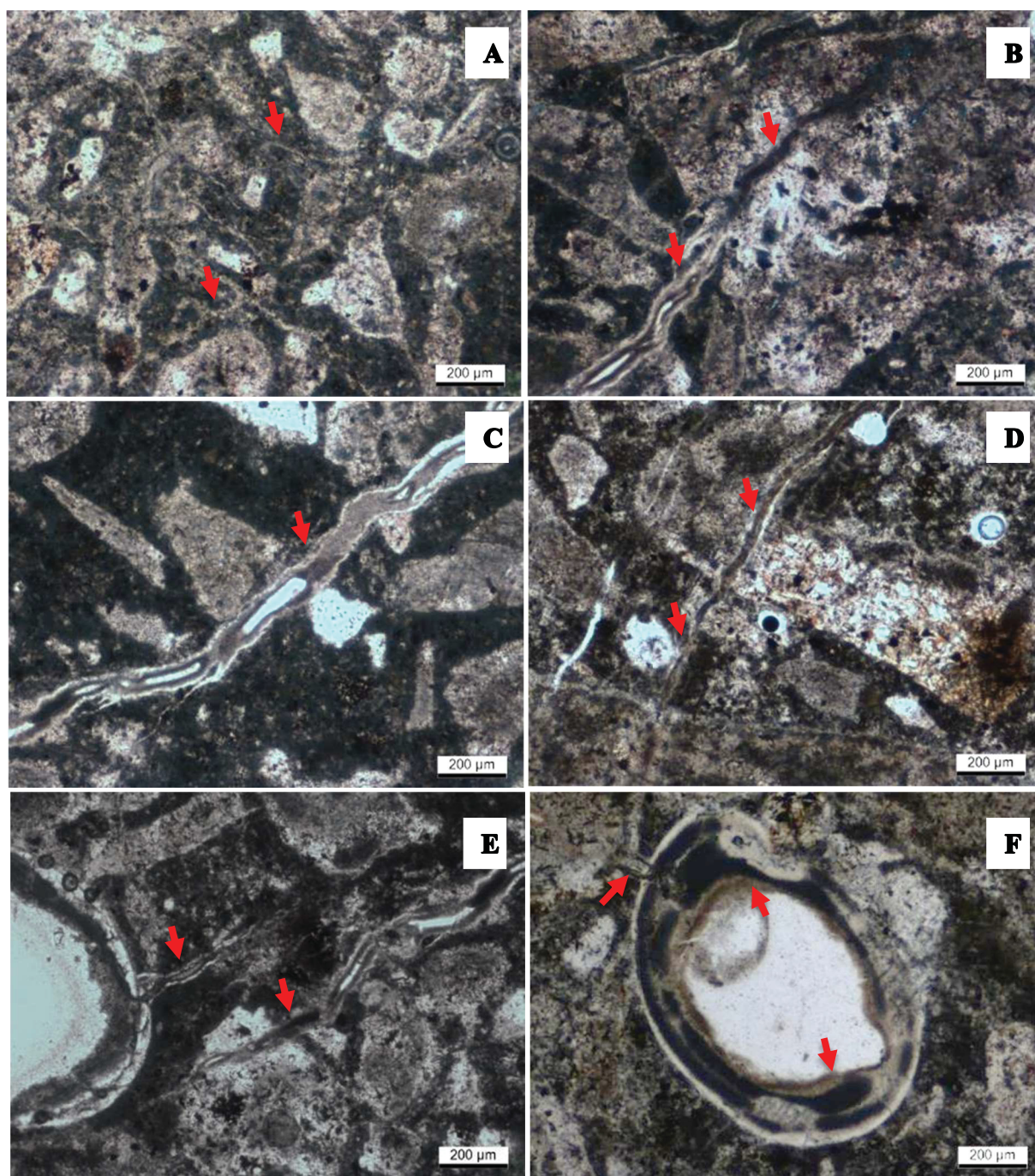


Figure 5.127. Photomicrographs of MOZ mortar. All photos in PPL. A) Very fine cracks in the cement paste; B) Crack filled with gel within the rhyolite particle that extends into the cement paste, where it is lined by gel; C) The extension of the same crack shown in B), crossing the cement paste and cutting some aggregate particles; D) Another crack within the rhyolite particle with gel that extends into the cement paste and crosses another aggregate particle; E) Cracks, one extending to the pore and another crossing an aggregate particle, both containing gel; F) Pore connected with a rhyolite particle by a crack.

Norway

The NOR mortar contains basaltic crushed aggregates. The texture and mineralogy are the same as described in section 5.22.

The NOR mortar presents very few and minor cracks in the cement paste (Figure 5.128A). In some aggregate particles, isotropic brown material was observed filling cracks inside aggregate particles but usually do not extend into the cement paste (Figure 5.128B), except for one of the cracks (Figure 5.128C).

The majority of the small voids are filled or lined by brownish material that could be polishing material or secondary products (Figure 5.128D). There is no evidence for an ongoing ASR in the mortar.

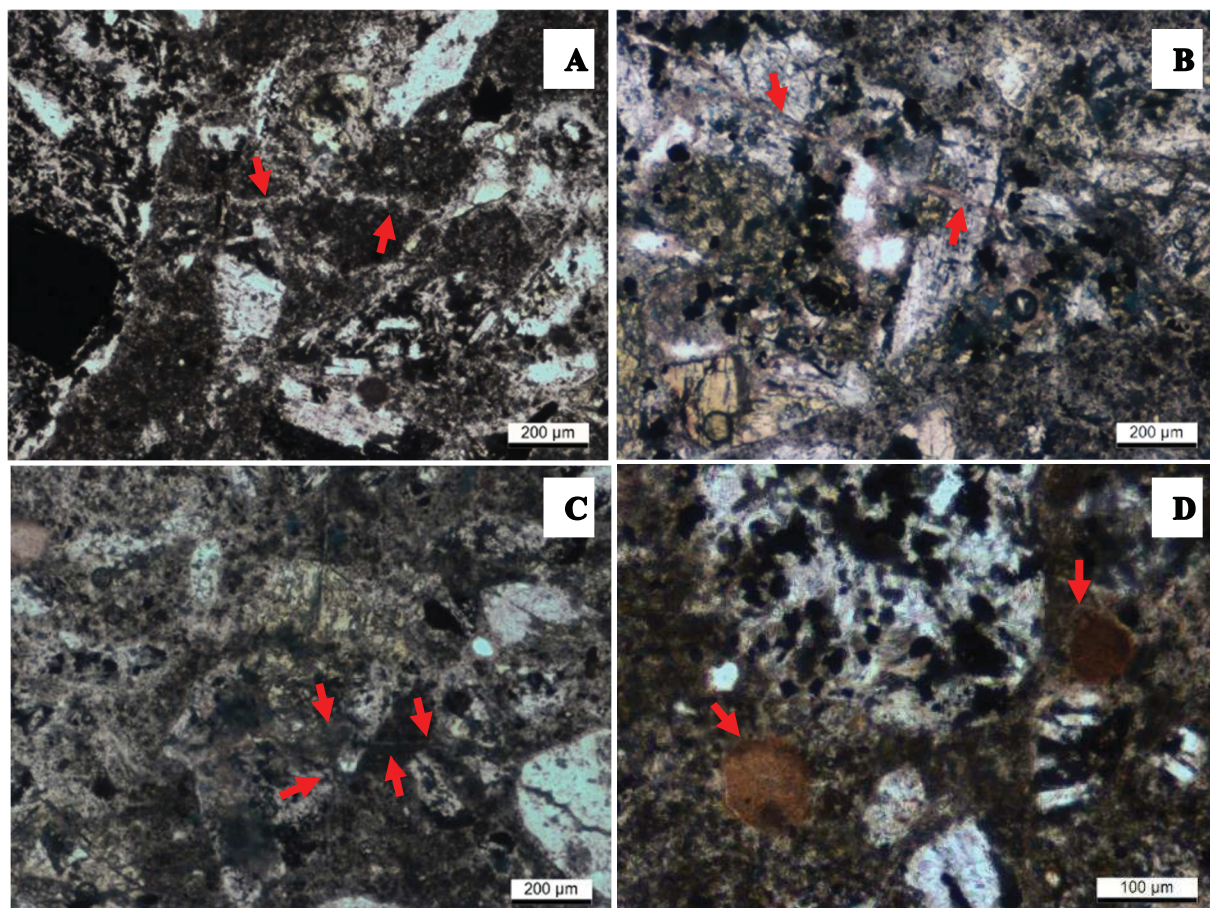


Figure 5.128. Photomicrographs of NOR mortar. All photos in PPL. A) Minor cracks in the cement paste; B) Crack with a brownish material within a basaltic particle; C) Cracks with a brownish material within a basaltic particle that extended into the cement paste; D) two pores filled with brownish material.

Turkey

The TK mortar was manufactured with andesitic crushed aggregate. The texture and mineralogy are described in section 5.22.

The TK mortar shows several cracks in the aggregate particles (Figure 5.129A and B), some are quite wide and partly filled with gel. These cracks have continuity to the cement paste and connect to other aggregate particles by crossing them (Figure 5.129C, D and E). Some particles are outlined by gel, filling the interface with the cement paste (Figure 5.129F). Some voids are lined by gel or ettringite.

There is a strong evidence for an ongoing ASR in the mortar bar, where several andesitic aggregate particles are responsible for the reaction, with formation of alkali-silica gel.

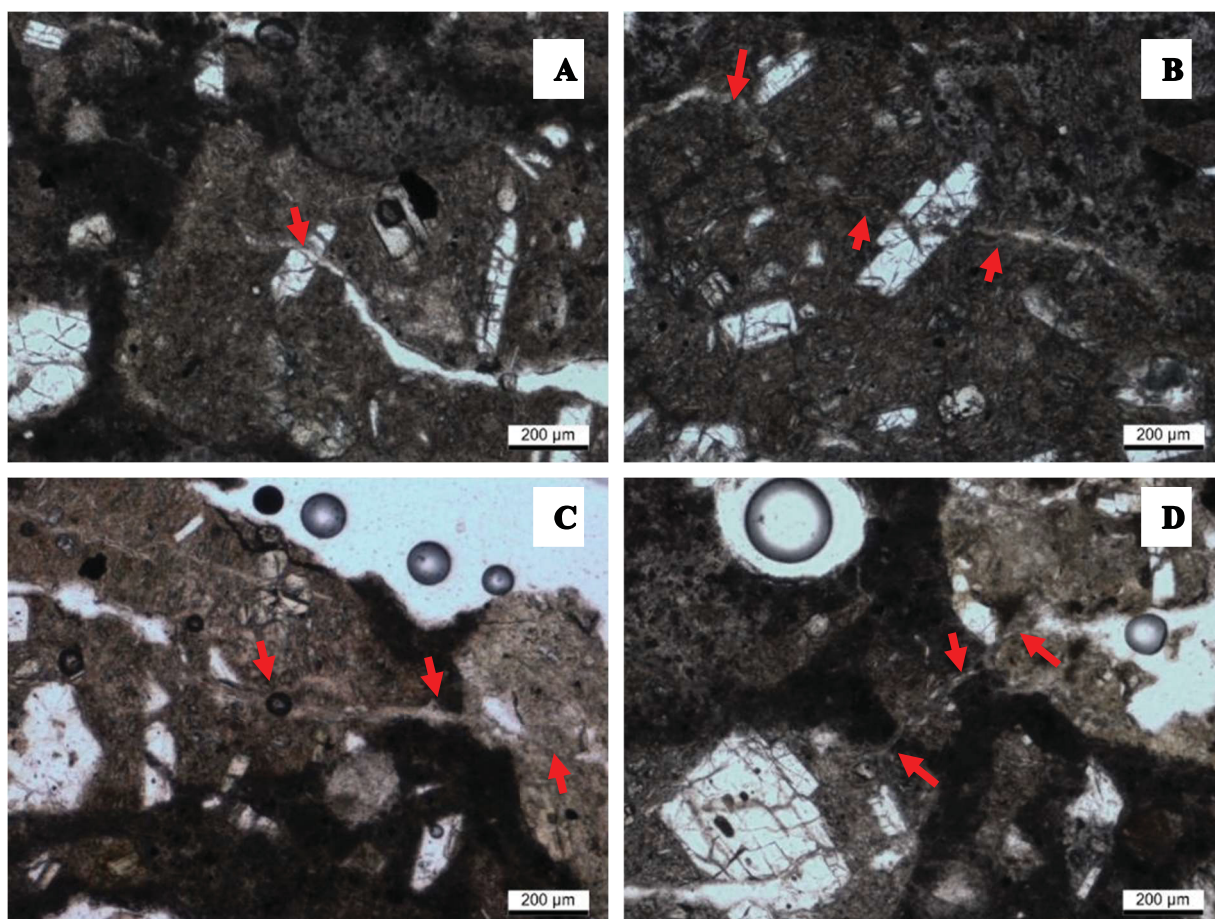


Figure 5.129. Photomicrographs of TK mortar. All photos in PPL. A) Large crack within the aggregate particle partly filled with gel; B), C), D) Cracks with gel within the aggregate particles extending into the cement paste and connecting to other particles.

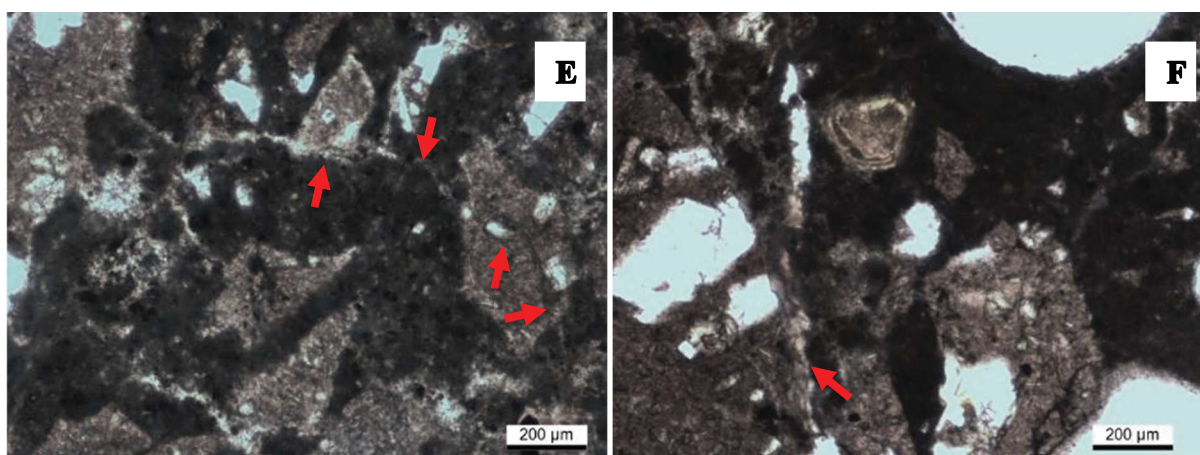


Figure 5.129. (continued). Photomicrographs of TK mortar. All photos in PPL. E) Cracks with gel within the aggregate particles extending into the cement paste and connecting to other particles; F) Gel in the interface of the aggregate particle with the cement paste, with continuity into the cement paste.

5.2.3. Concrete studies

5.2.3.1. Expansion tests - Concrete prism test at 38°C (CSA A23.2-14A, 2015)

A number of concrete prism tests were performed. Thirty-one mixes were prepared at the Université Laval, in Québec, Canada. The mixes that contain the aggregates from Continental regions (BRAZ, CAN, MOZ, NOR and TK) are the same as for the AMBT. Spratt and also GBS sand are used as references in each figure. The characteristics of the concrete are the same as presented in Table 4.13 in chapter 4. The CPT method is described by the CSA A23.2-14A (2015), ASTM C 1293 (2020) and RILEM AAR-3 (2016) but the limits are provided by the CSA Standard Practice A23.2-27A (2019), ASTM C 1778 (2020) and RILEM AAR-0 (2016).

Brazil

The results of the CPT for BRAZ aggregate show only negative expansion, not reaching the limit values.

According to the limits of expansion indicated in the different standards (CSA 23.2-27A, 2019; ASTM C 1778, 2020) and RILEM recommendations, this aggregate is considered non-reactive. The results for the CPT method for the BRAZ aggregate are shown in Figure 5.130.

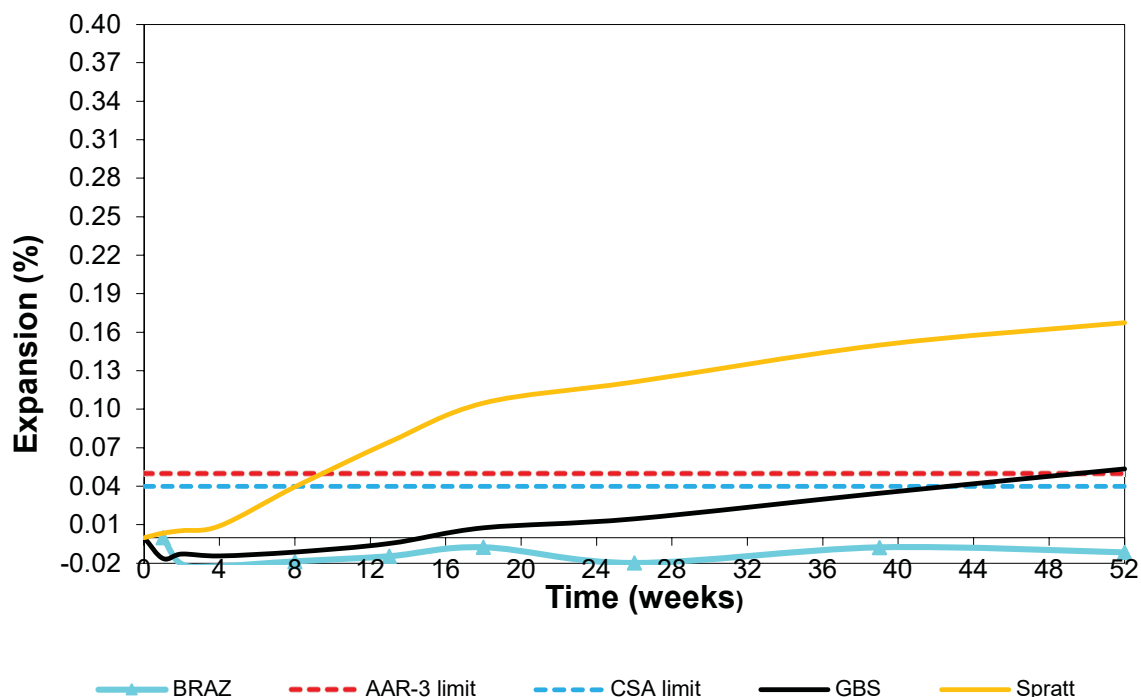


Figure 5.130. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the BRAZ aggregate.

Canada

The concrete prisms made with aggregate CAN show very low expansion. At the end of one year of testing, the expansion value is only 0.006%. The expansion presented always negative values but at week 39 the value passed to positive numbers, still maintaining very low expansions and not reaching the threshold.

The results obtained classify this aggregate as non-reactive, in accordance to the expansion limits for the American and Canadian standards ($< 0.040\%$) and for the RILEM recommendations ($< 0.05\%$).

The results for the CPT method for the aggregate CAN are shown in Figure 5.131.

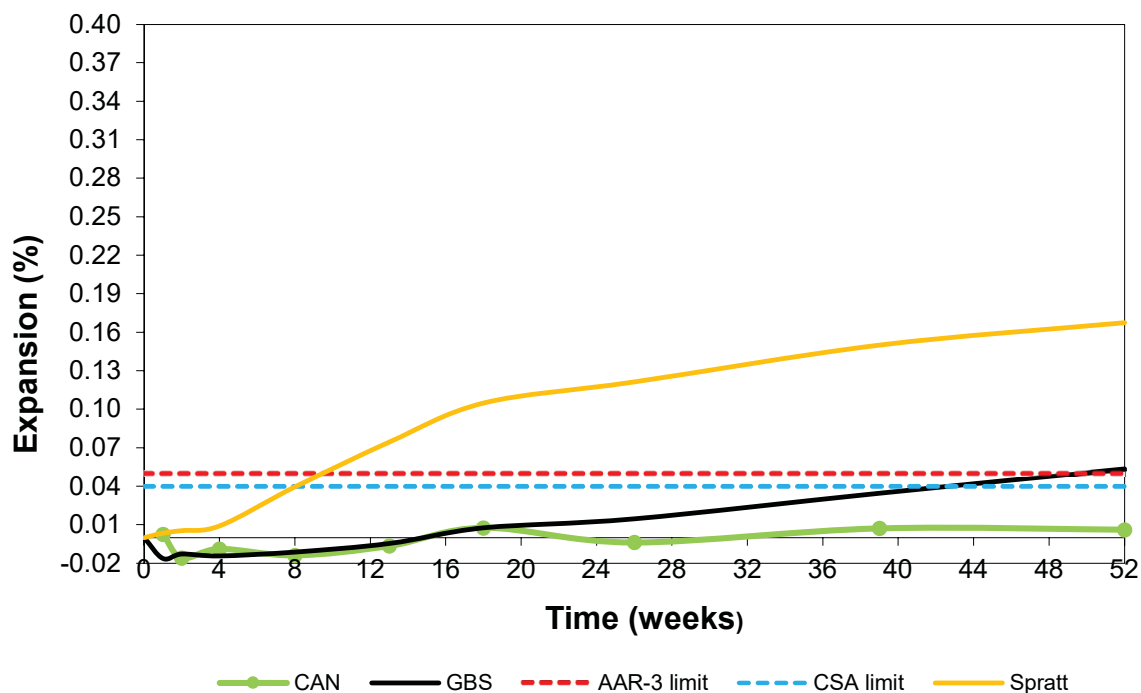


Figure 5.131. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the CAN aggregate.

Mozambique

The aggregate MOZ shows very low expansion in the CPT. At the end of one year of testing, the expansion value is only 0.004%. The expansion values showed some variations between negative values and zero expansion. The expansion started to increase only at week 39 with 0.003% but still maintained very low level and not reaching the limit values.

The results obtained classify this aggregate as non-reactive, in accordance to the expansion limits for the American and Canadian standards ($< 0.040\%$) and for the RILEM recommendations ($< 0.05\%$).

The results for the CPT method for the aggregate from MOZ are shown in Figure 5.132.

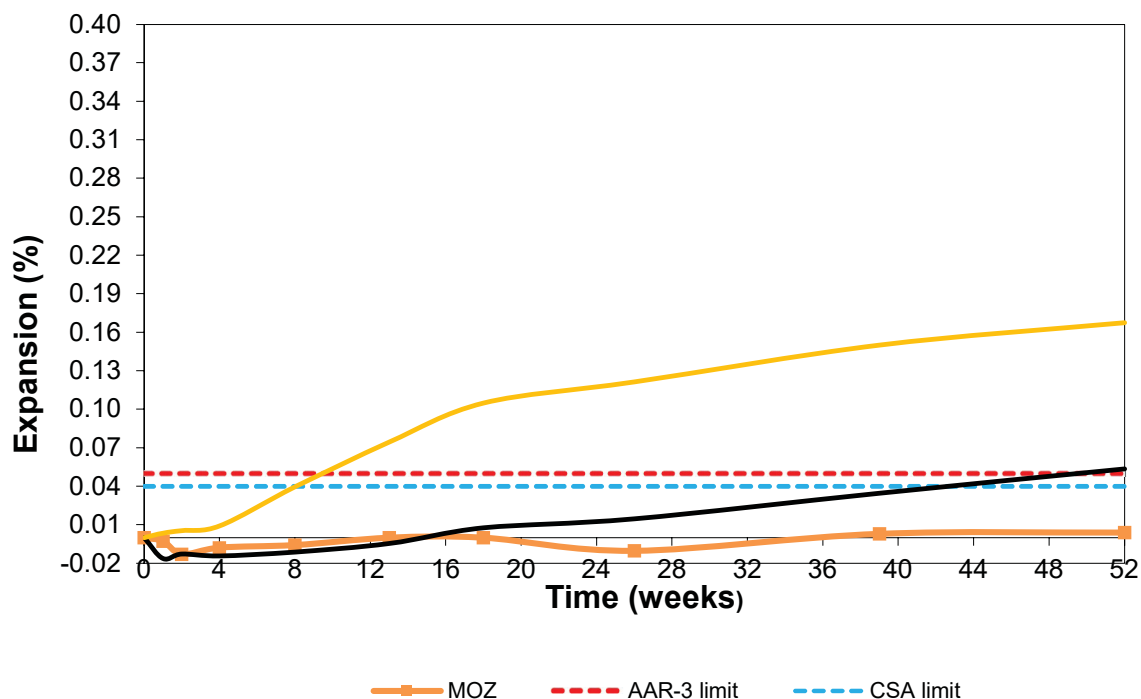


Figure 5.132. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the MOZ aggregate.

Norway

The concrete prisms containing the aggregate NOR show very low expansion. At the end of one year of testing, the expansion value is 0.002%. The values showed some variations between positive and negative expansion. The measure done at the 1st week of testing showed that the expansion increased to 0.003%. After the 2nd week, the values were negative until week 39 where expansion increased to 0.001%. After that, the expansion only increased 0.001% between week 39 and week 52. Overall, the prisms maintained very low expansion not reaching the threshold.

The results obtained classify the aggregate as non-reactive, in accordance to the expansion limits for the American and Canadian standards (< 0.040%) and for the RILEM recommendations (< 0.05%).

The results for the CPT method for the aggregate from NOR are shown in Figure 5.133.

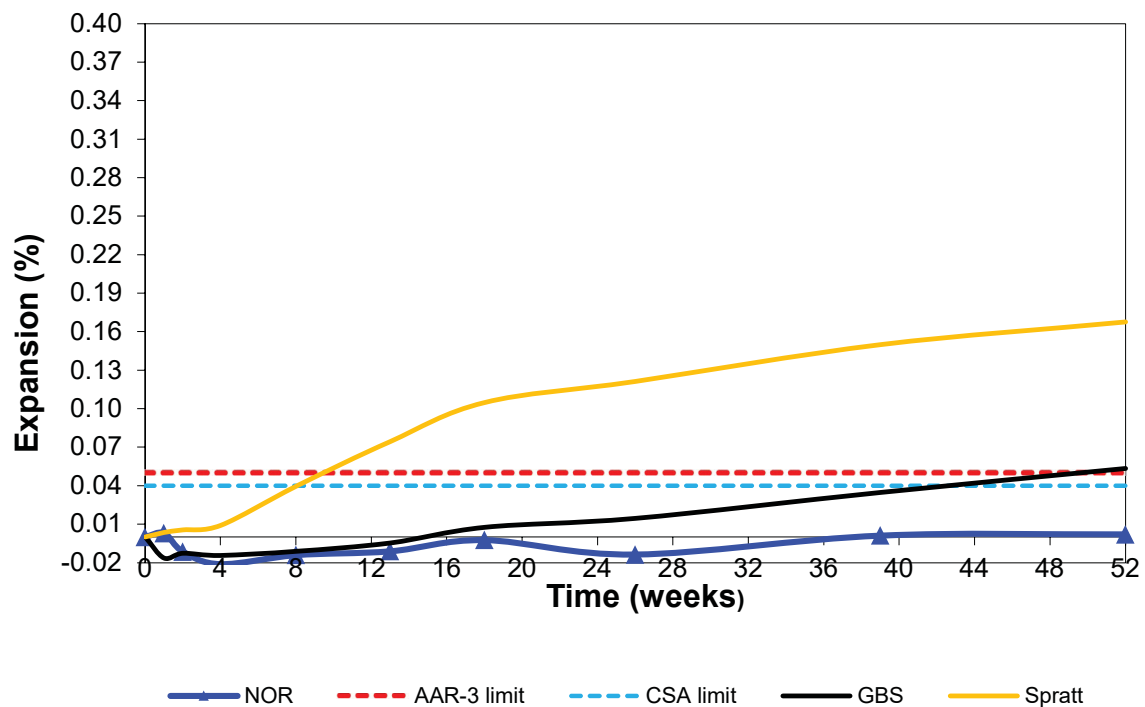


Figure 5.133. Expansion results of the CPT method test at 35°C (CSA A23.2-14A, 2015) concerning the NOR aggregate.

Turkey

The concrete prisms prepared with the TK aggregate show moderate expansion. At the end of one year of testing the expansion value is 0.144%. The expansion started to increase around week 4. And at week 18 some tendency for stabilization was noticed, although expansion continued to increase until the end of the testing. The result obtained for this aggregate classifies it as highly reactive, in accordance to the expansion limits for the American standard ($\geq 0.12\%$ - $< 0.24\%$), and for the Canadian standards ($\geq 0.120\%$ - $< 0.260\%$) and for the RILEM recommendations ($> 0.10\%$) it is considered an expansive material.

The results for the CPT method for the aggregate from TK are shown in Figure 5.134.

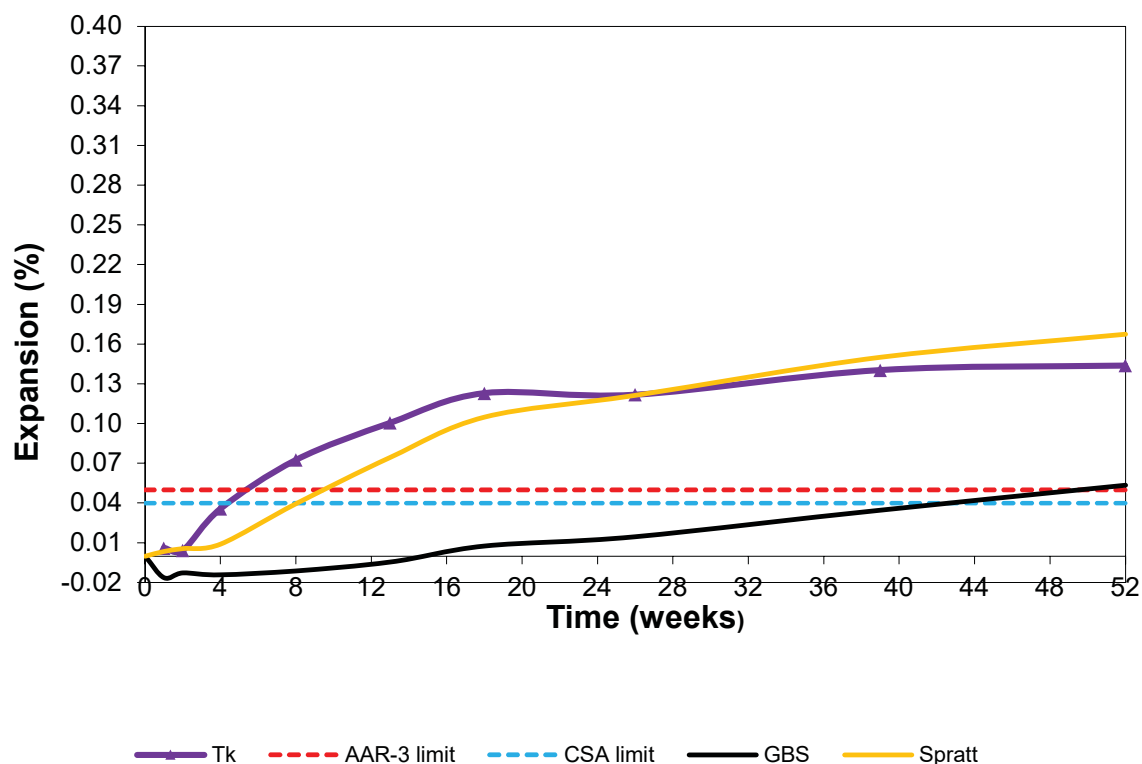


Figure 5.134. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the TK aggregate.

Spratt (Canada)

The concrete prism prepared with the Spratt aggregate show high expansion. The graph shows that at week 4 the expansion started to increase. At week 18 some stabilization is observed although the expansion continued to increase until the end of the testing. The expansion value obtained for one year of testing is of 0.168%; this is within the range of what is expected with that reference aggregate at about 0.16% at one year. Accordingly, it is classified as highly reactive according to CSA A23.2-27A.

The results for the CPT method for the aggregate from TK are shown in Figure 5.135.

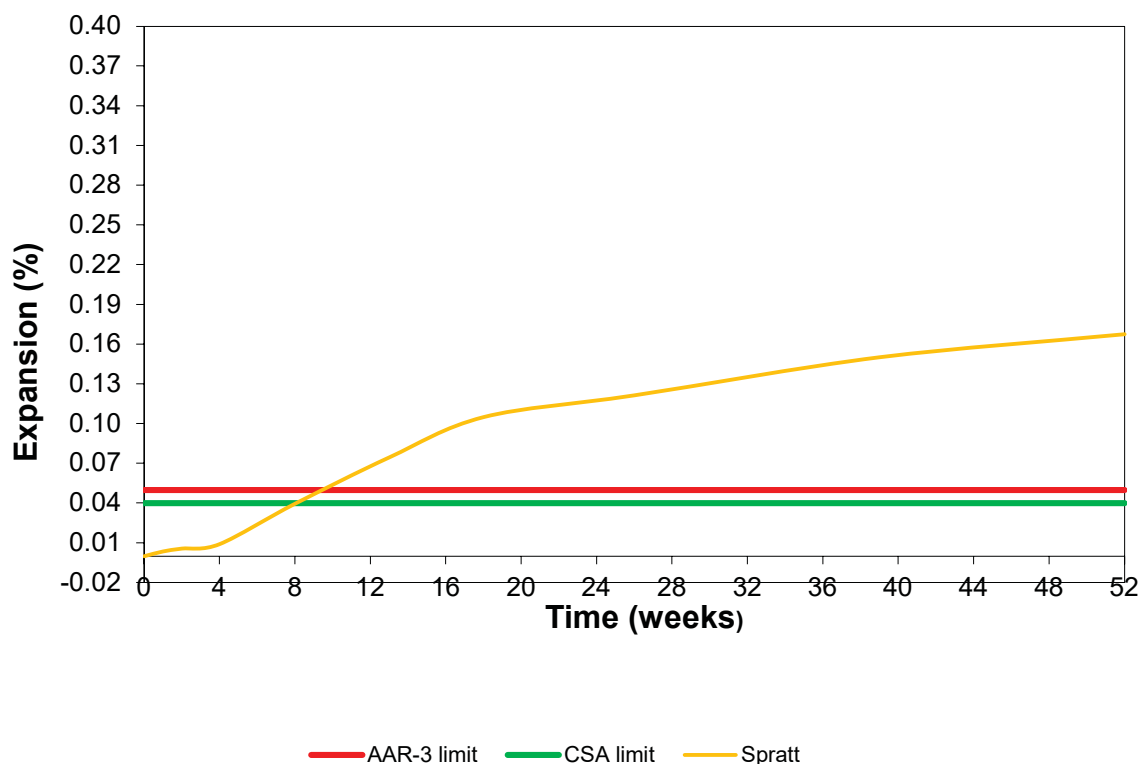


Figure 5.135. Expansion results of the CPT method test at 38°C (CSA A23.2-14A, 2015) concerning the SPRATT aggregate.

5.2.3.2. Gel Pat Test

The Gel Pat Test was performed for all concrete prisms from Continental regions. The procedure was done in the same way as for the concrete from the Ocean Islands. The test was performed during 19 weeks and photos obtained at 2, 4, 9 and 19 weeks. The quantity of gel produced in each concrete slab and at different periods of time allows to classify the ASR intensity into different categories: 0 = no gel, 1 = traces, 2 = some, 3 = fair, 4 = large and 5 = very large.

The results of GPT are presented in Table 5.43.

Figures 5.136 (A-F) and 5.137 (A-F) show the aspect of the different polished concrete sections at week 19 in general view and in detail.

The polished concrete section with BRAZ aggregate shows the presence of gel, with several aggregate particles showing small white deposits of gel (Figure 5.136A and B).

The concrete section from CAN aggregate shows no gel on the aggregate particles but some white dots are present in the cement paste (Figure 5.136C and D).

The reference concrete with Spratt aggregate shows a fine white film covering all the section (Figure 5.136E); in the aggregate particles, white deposits aligned along cracks are visible (Figure 5.136F) and gel is present on several aggregate particles.

The concrete with MOZ aggregate is covered by a whitish film (Figure 5.137A) and also white spots of gel are observed in different parts of many aggregate particles (Figure 5.137B).

The concrete section containing NOR aggregate does not show a white film and there is no gel (Figure 5.137C), however there are very few white deposits in the cement paste (Figure 5.137C and D).

The TK concrete section shows a whitish film covering the surface; several aggregate particles show abundant white dots (Figure 5.137E and F).

Table 5.43. Results of the GPT after 19 weeks of testing

Samples	GPT (19 w)	Description
BRAZ	3	With gel
CAN	0	No gel
MOZ	5	Gel on many particles; whitish film
NOR	0	No gel
TK	5	Gel on many particles; whitish film
Spratt	2.5	Gel on several particles, often with deposits aligned along cracks; +/- whitish film
GBS	2	Gel on several particles of the sand fraction; no whitish film
0=no gel; 1=traces; 2=some; 3=fair; 4=large; 5=very large		

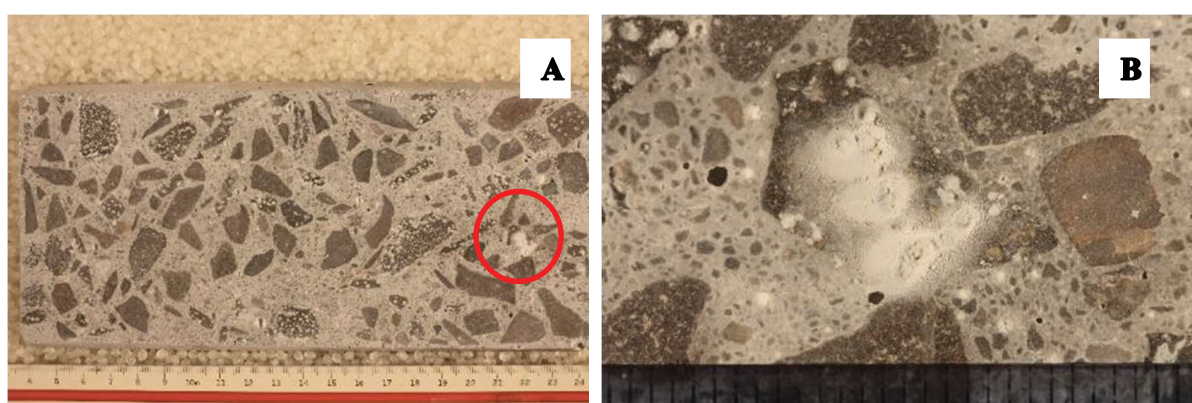


Figure 5.136. GPT performed in different polished concrete sections at week 19. A) concrete section with BRAZ aggregate; B) Detail of one aggregate particle (BRAZ).

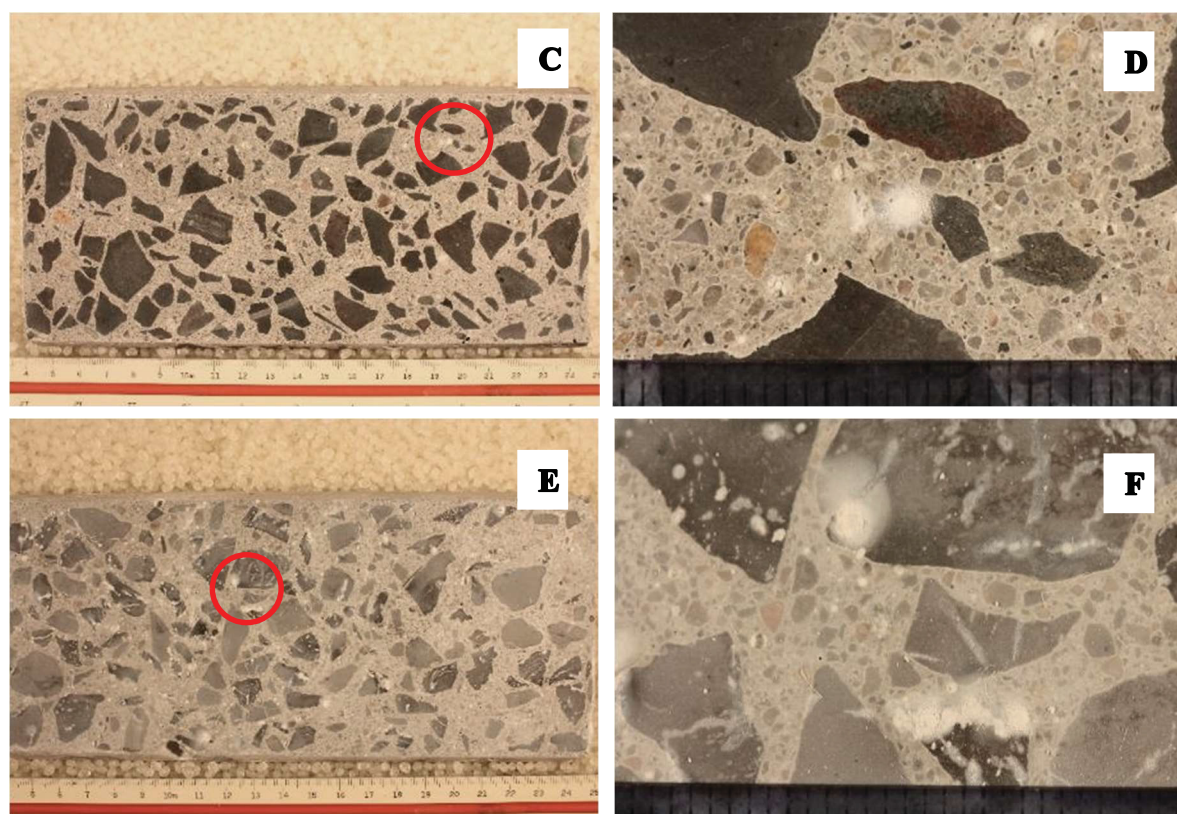


Figure 5.136 (continued). GPT performed in different polished concrete sections at week 19. C) Concrete section with CAN aggregate; D) Detail of the cement paste (CAN); E) Concrete section with Spratt aggregate; F) Detail of the concrete (Spratt).

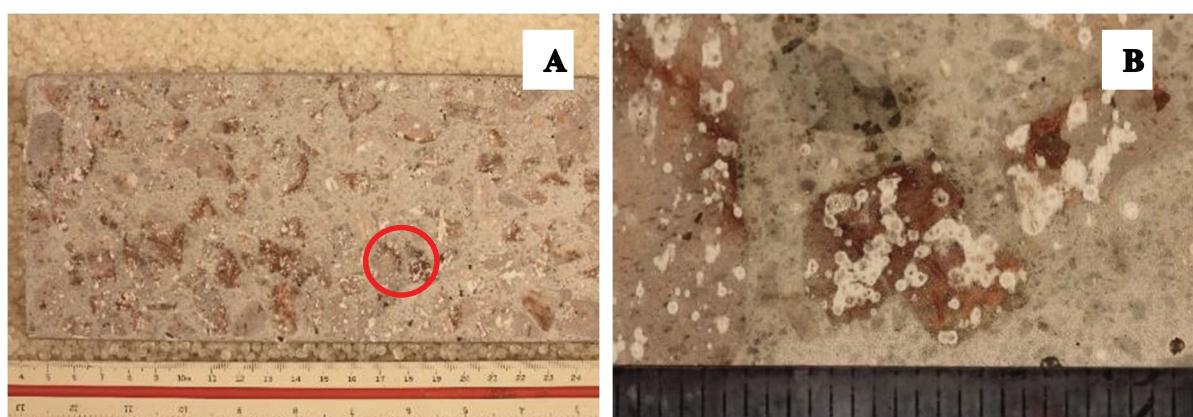


Figure 5.137. GPT performed on different polished concrete sections at week 19. A) concrete section with MOZ aggregate; B) Detail of some aggregate particles (MOZ) with deposits of gel

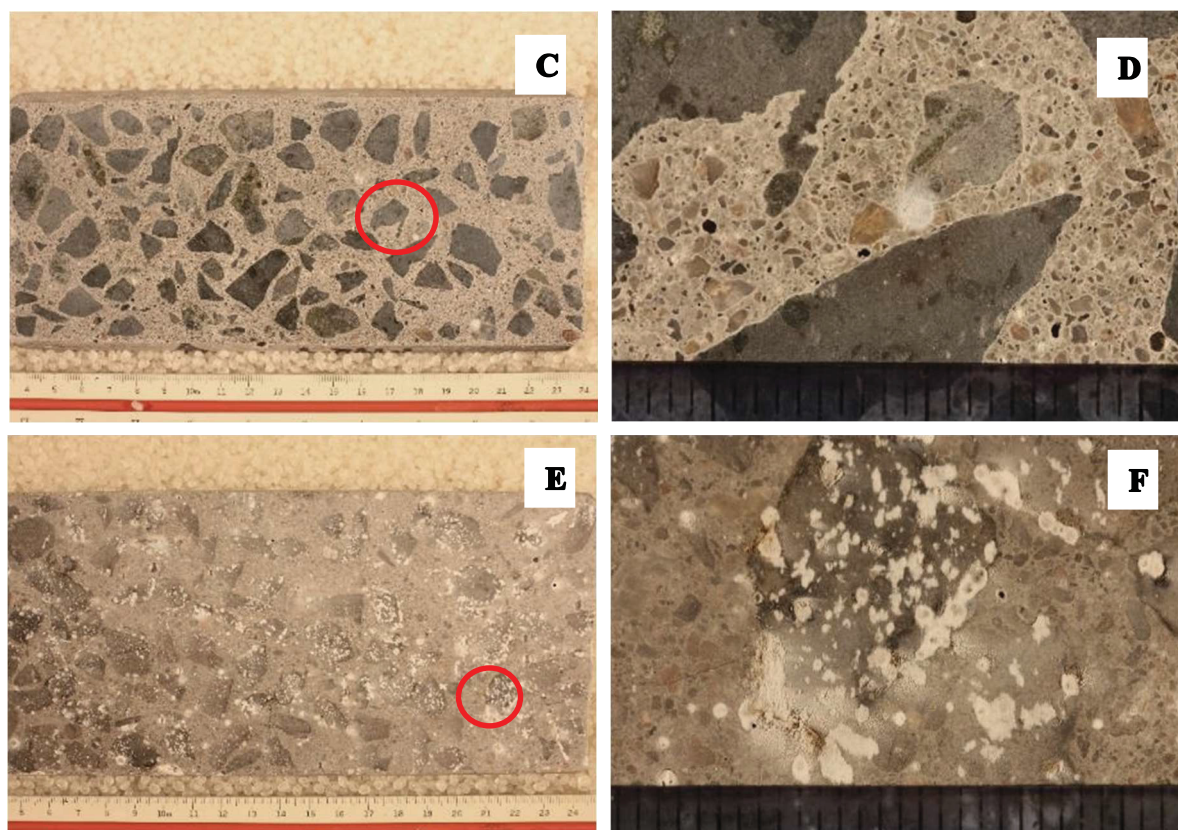


Figure 5.137 (continued). GPT performed on different polished concrete sections at week 19. C) Concrete section with NOR aggregate; D) Detail of the cement paste (NOR); E) Concrete section with TK aggregate; F) Detail of the concrete (TK) with extensive deposits of gel on one of the aggregate particles.

5.2.3.3. Petrographic examination - Damage Rating Index (DRI)

The DRI was performed on concrete polished sections incorporating the BRAZ, Spratt, MOZ and TK concrete prisms. It was chosen not to perform the DRI on the CAN and NOR concrete prisms due to the low expansion obtained in the CPT method and also because of the GPT results. The DRI results are shown in Tables 5.44 and 5.45.

The DRI method showed that the concrete with TK aggregate, when compared to the other concretes from Continental regions, with the exception of Spratt, was the one with more closed and opened cracks in the aggregate particles, more reaction products in opened cracks, more debonded aggregate particles and more cracks in the cement paste filled, or not, with reaction products. It was noticed that the majority of the cracks within the aggregates were concentrated near the border of the particles. According to Table 5.45, the degree of ASR is severe to very

severe with severe signs of deterioration. Figures 5.138A, B, C and D show some deterioration features of TK concrete.

Table 5.44. Detailed results (number of counts multiplied by the weighing factors) of reaction features for each sample at the end of one year of testing.

Samples	CCA	OCA	CA+RP	Deb	RAP	CCP	CCP+RP	DRI
BRAZ	3	263	0	1	2	14	0	284
MOZ	16	12	3	0	0	6	0	37
TK	30	492	87	66	9	139	81	903
Spratt	67	761	215	17	9	28	172	1270
GBS	151	166	34	9	6	69	30	449

Table 5.45. Concrete condition and degree of deterioration based on the DRI results based on Villeneuve, (2011); Villeneuve et al. (2012); Fournier et al. (2015). Spratt and GBS area reference aggregates.

Samples	DRI	Degree of deterioration
BRAZ	284	Fair to moderate – Concrete generally in good condition
MOZ	37	Trace – Concrete in good conditions
TK	903	Severe to very severe - Concrete with severe signs of deterioration
Spratt	1270	Severe to very severe - Concrete with severe signs of deterioration
GBS	449	Moderate to severe - Concrete with moderate signs of deterioration

The concrete with BRAZ aggregate shows very few cracks in the cement paste but, in contrast, presents a high number of open cracks within the aggregate particles; however, those cracks are largely empty (i.e. no reaction products) (Figure 5.139A and B).

The concrete containing MOZ aggregate was the one showing the least petrographic features of deterioration. Some closed (Figure 5.140A) and open cracks (Figure 5.140B) in the aggregate particles were observed, with only a few containing reaction products and very few cracks in the cement paste, with no reaction products.

The concrete prepared with the Spratt aggregate shows a number of petrographic features of deterioration. These features include mainly open cracks with or without reaction products within the aggregate particles and cracks in the cement paste with reaction products (Figure 5.141A and B). Some voids are also filled with whitish reaction products, ASR gel (Figure 5.141C). In some cases, aggregate particles are debonded (Figure 5.141D).

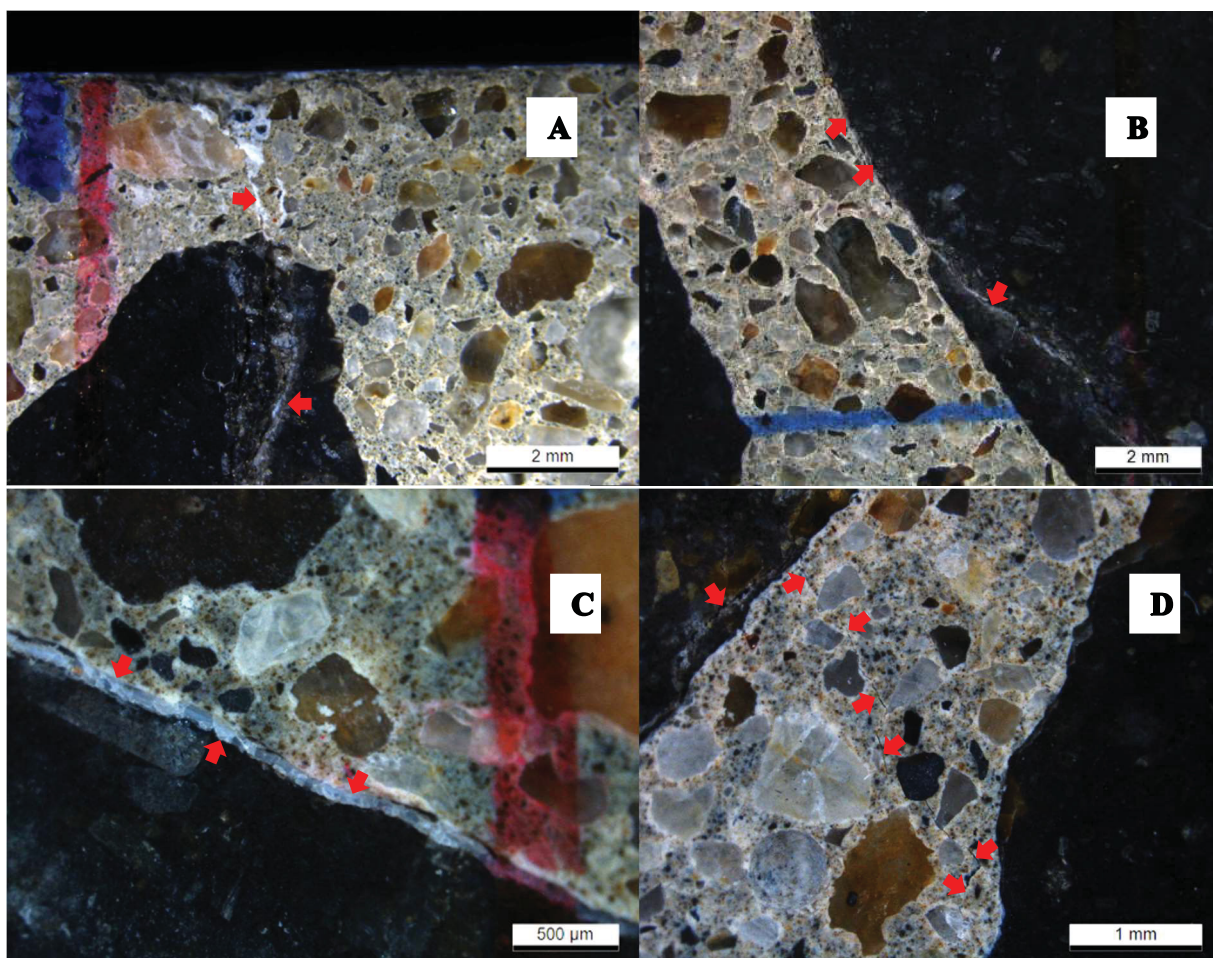


Figure 5.138. Photographs of TK concrete prisms observed under the stereobinocular microscope.

A) Open crack with some gel in an aggregate particle, extending into the cement paste; B) Open crack in an aggregate particle with reaction product and outlining the particle (red arrows); C) an aggregate particle with a rim of gel filling the interfacial zone with the cement paste; D) cracks in the cement paste and in one of the aggregate particles.

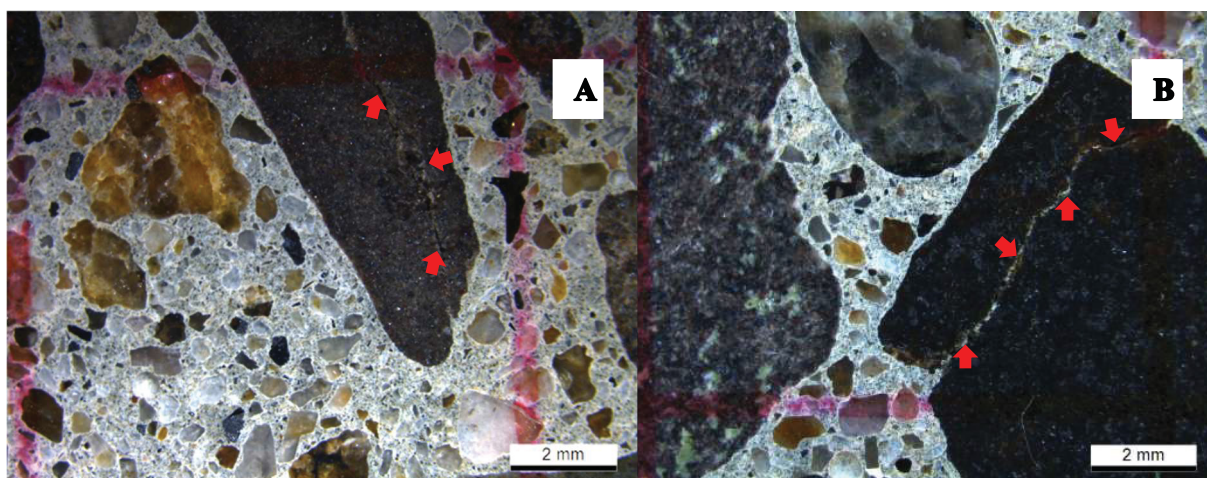


Figure 5.139. Photographs of BRAZ concrete prism. A) Open crack within the aggregate particle (red arrows); B) Open crack within another aggregate particle.

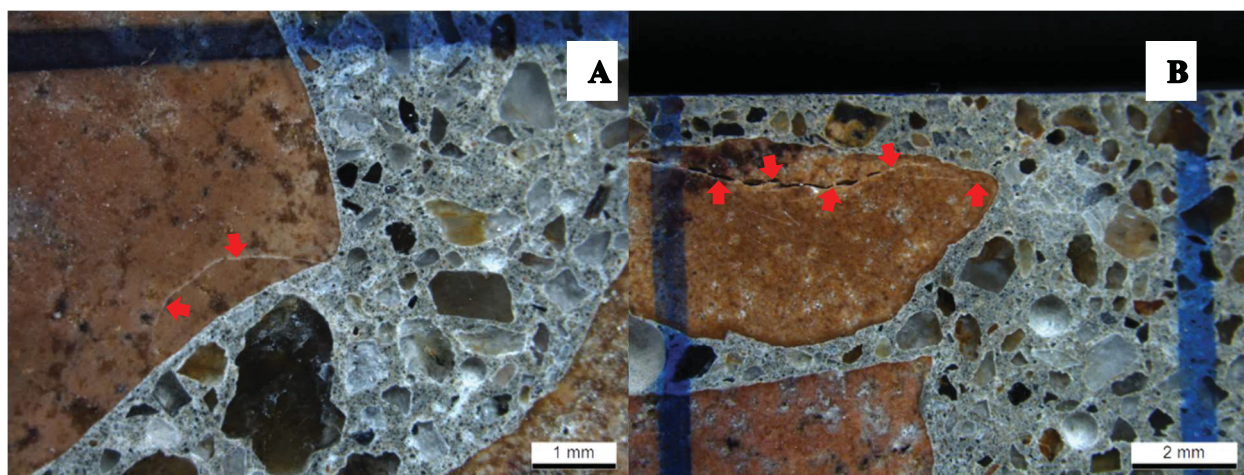


Figure 5.140. Photographs of MOZ concrete prism. A) Closed crack within the aggregate particle (red arrows); B) Open and closed crack (red arrow in the right) within the aggregate particle.

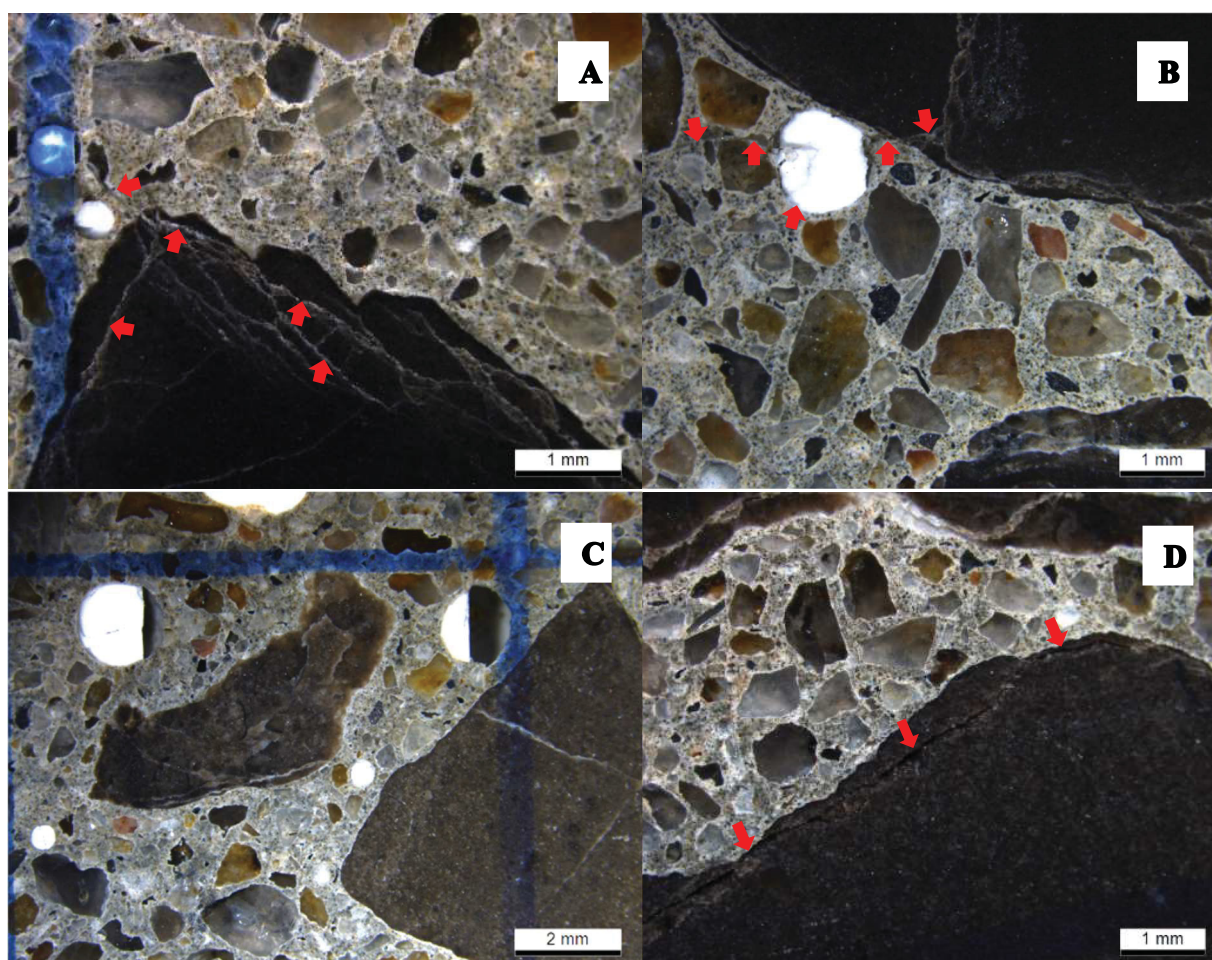


Figure 5.141. Photographs of Spratt concrete prisms. A) Several cracks within an aggregate particle that extend into the cement paste, containing reaction product in both places (red arrows); B) Crack with reaction product within an aggregate particle that continues to the cement paste and connects to a void filled with ASR gel; C) different voids with ASR gel; D) Debonded aggregate particle and crack inside the particle (red arrows).

5.2.3.4. Post-mortem petrography

All the concrete aggregates from Continental regions correspond to crushed rocks. The sand used was the same for all aggregates and consists of a non-reactive natural sand incorporating feldspar (alkali feldspar and plagioclase) with intergrowth (perthite) and reaction textures (myrmekite), some grains of microcline, quartz, clinopyroxene (aegirine-augite), opaque minerals and biotite. Also, some of the grains of the sand fraction are formed by microcrystalline quartz. For all the concrete prisms, the cement paste is homogeneous. The concrete petrography was not done for the CAN and NOR aggregates due to the low expansion obtained in the CPT and the results obtained in the GPT.

Brazil

The BRAZ basalt aggregate shows the same mineralogy and texture described in 5.22.

In general, there are some cracks in the cement matrix that connect the aggregate particles, either cross or surround some grains of the sand fraction (Figure 5.142A and B) and connect to air voids. Although most of them are empty, it was observed some dark material filling partly the cracks in small different sections of the aggregate particles or surrounding them (Figure 5.142C and D, E, E and F). In the aggregate particles, there are very few cracks and usually they are filled with calcite. The majority of the voids are empty and very few are lined with a brownish secondary product that is thought to correspond to gel.

There is a slight evidence for an ongoing ASR in the concrete prism, although there are very few fine cracks in the aggregate particles. The brownish secondary product that is thought to correspond to gel appears only in some cracks in the cement paste.

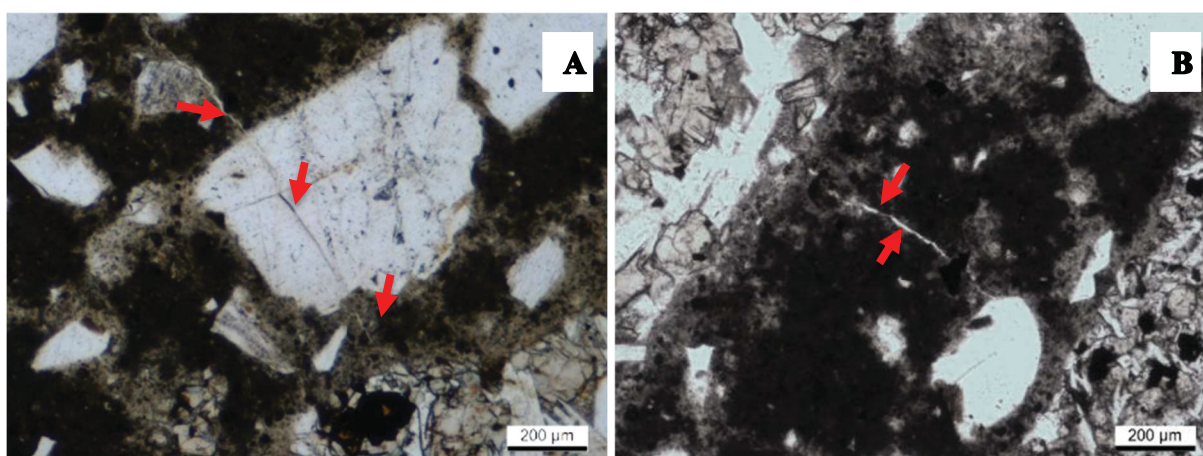


Figure 5.142. Photomicrographs of BRAZ concrete prism. All photos in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction.

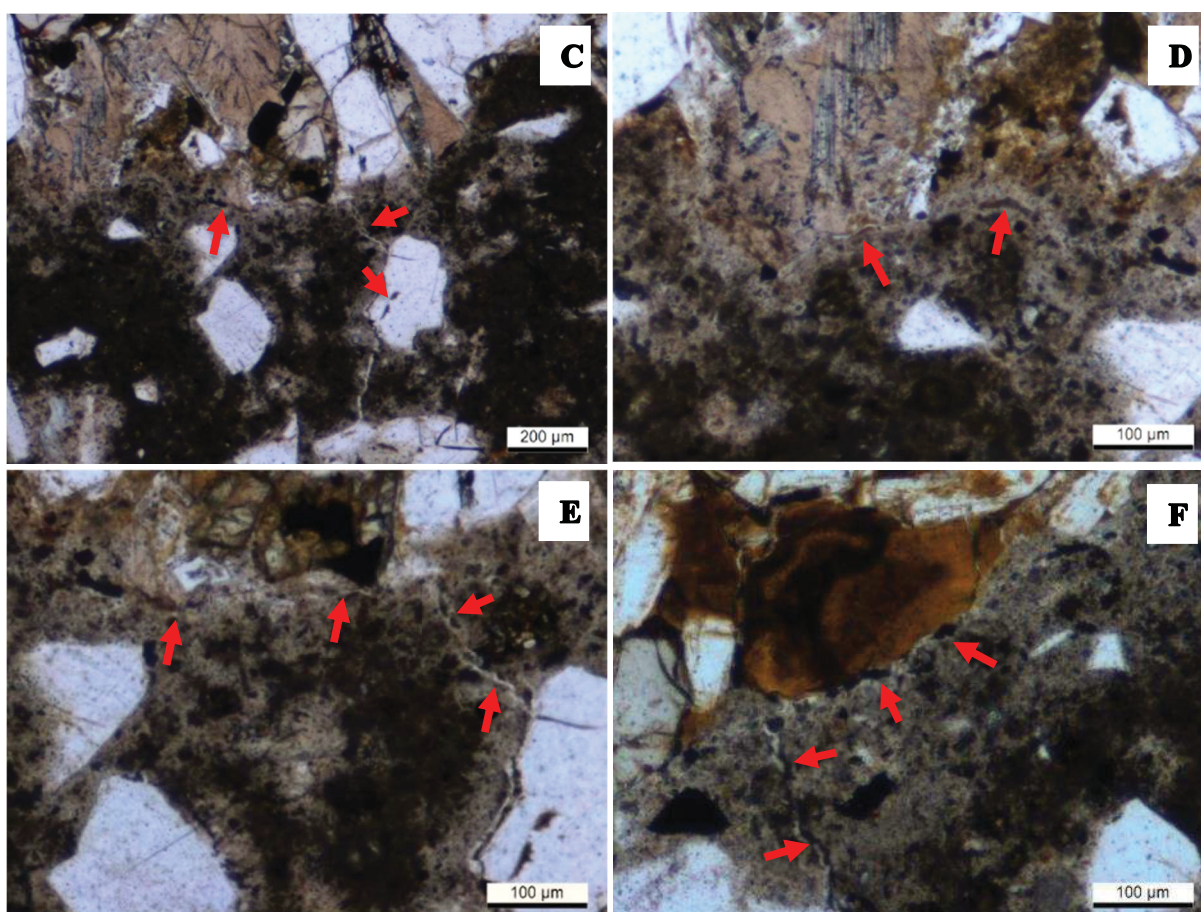


Figure 5.142 (continued). Photomicrographs of BRAZ concrete prism. All photos in PPL. C), D), E) and F) tiny cracks with brownish material (gel?) in the interfacial zone between the aggregate particles and the cement paste and extending into the cement paste.

Spratt (from Canada)

Spratt is composed of siliceous limestone. Some aggregate particles contain carbonate and siliceous bioclasts, while others are mainly formed by calcite and others contain a reddish-brown material (probably clay minerals and limonite) in the rock matrix.

The concrete thin section revealed the presence of several cracks in the cement paste (Figure 5.143A, B), some of which are long and others are thin and short. The cracks often surround the grains of the sand fraction. The presence of a brownish material is noticed filling partly the cracks in the cement paste (Figure 5.143C) and sometimes outlining the aggregate particles. Small voids are partly or filled with brownish material (gel?) (Figure 5.143D).

There is some evidence for an ongoing ASR in the present concrete, where the siliceous limestone particles are responsible.

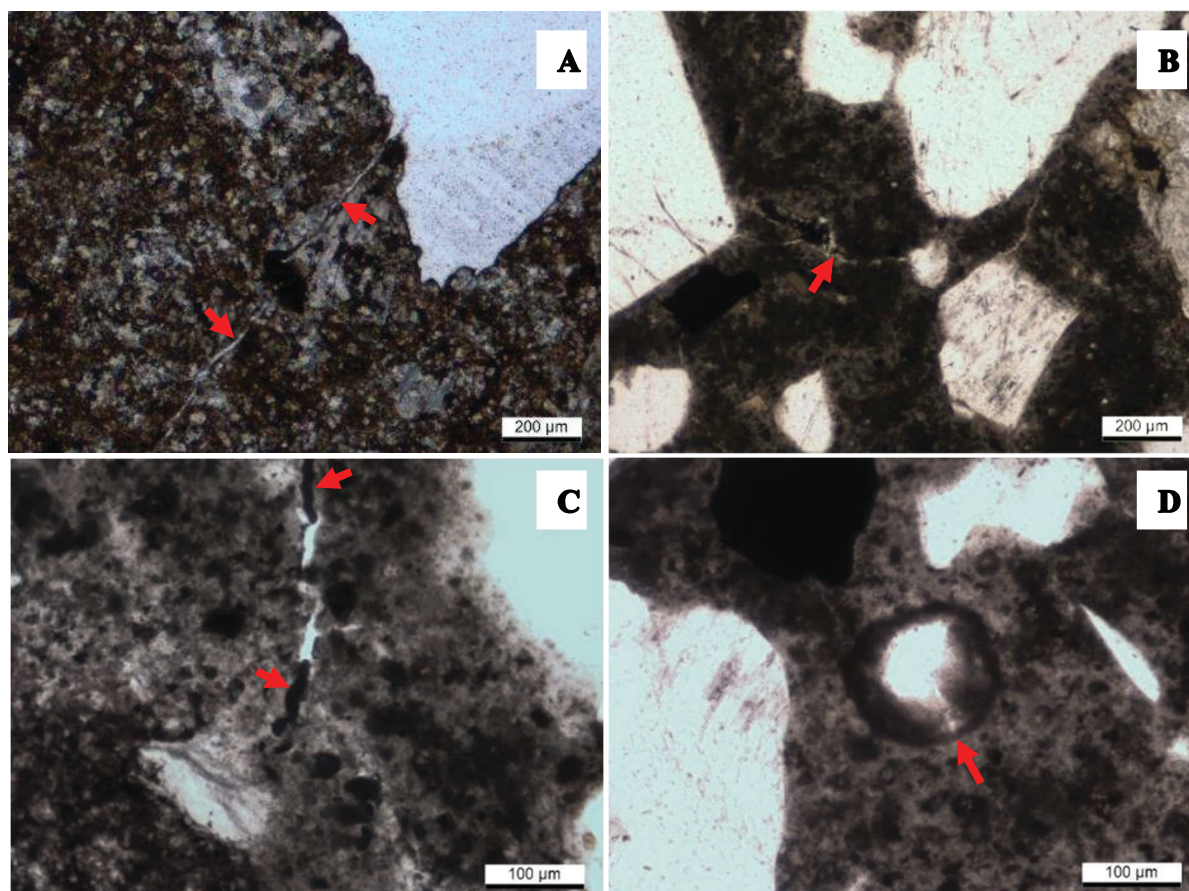


Figure 5.143. Photomicrographs of Spratt reference concrete prism. All photos are in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction; C) Cracks with brownish material in the cement matrix; D) Void partly filled with brownish material (gel?).

Mozambique

The aggregate is a rhyolite, as described in 5.22.

In general, there are several cracks in the cement paste but they are not filled with gel (Figure 5.144A and B). Some cracks are outlining the aggregate particles (Figure 5.144C). There are no cracks in the aggregate particles and the voids are empty (Figure 5.144D).

There is no evidence for an ongoing ASR in the present concrete.

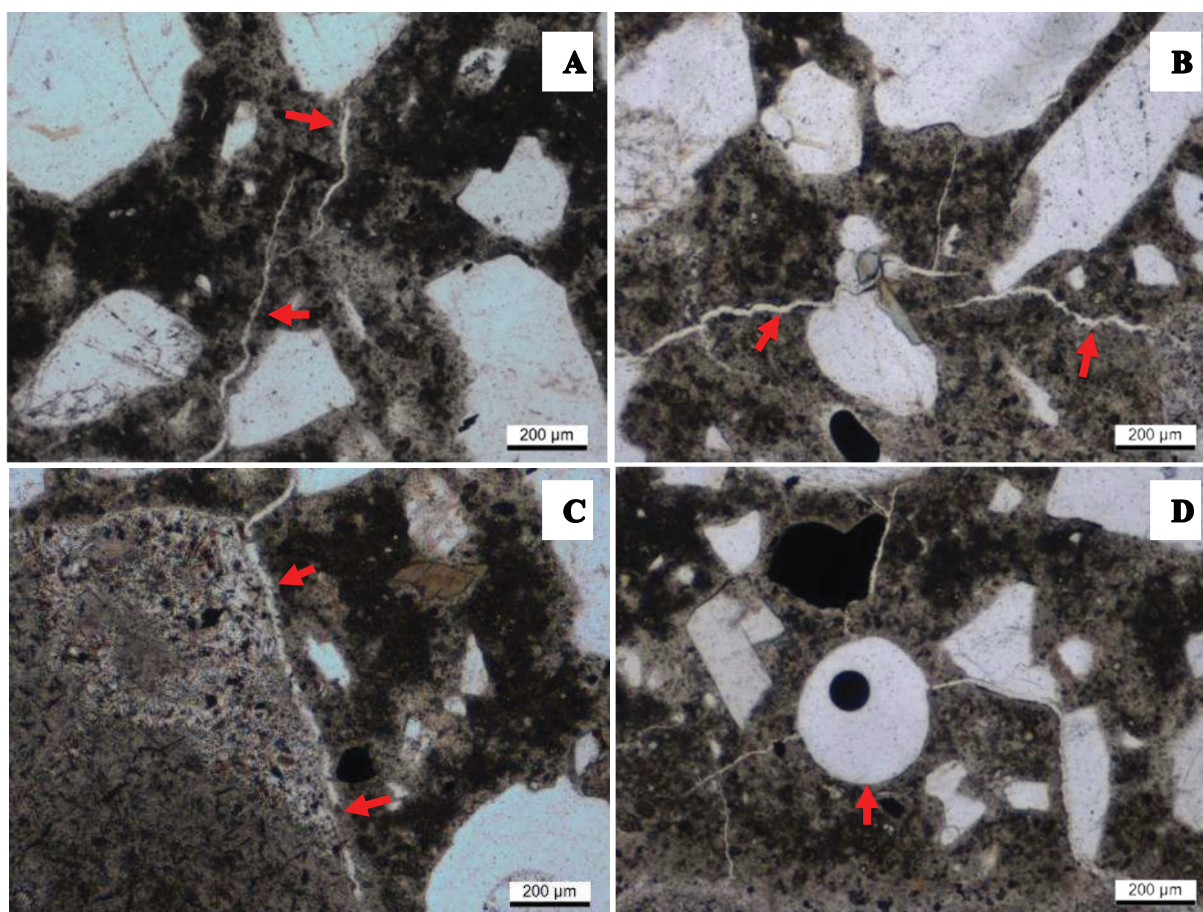


Figure 5.144. Photomicrographs of MOZ concrete prism. All photos are in PPL. A) and B) Cracks in the cement matrix connecting some grains of the sand fraction; C) Cracks in the interface zone between an aggregate particle and the cement matrix; D) Very fine cracks in the cement paste and an empty void.

Turkey

The aggregate is composed of andesites that have the same mineralogy and texture as described in 5.22.

In general, most of the aggregate particles are surrounded by brownish material (Figure 5.145A). There are some cracks in the cement paste connecting the aggregate particles that are also crossing or surrounding some particles of the sand fraction (Figure 5.145B) or linking to air voids. Within the aggregate particles, the cracks are located near the border of the particle (Figure 5.145C). In one of the aggregate particles, there is a cracked yellow-brownish material located at the boundary between the particle and cement paste. Some parts are isotropic, others maintain the yellow-brownish colour (Figure 5.145D, E and F). Some of the air voids are lined with a brownish material.

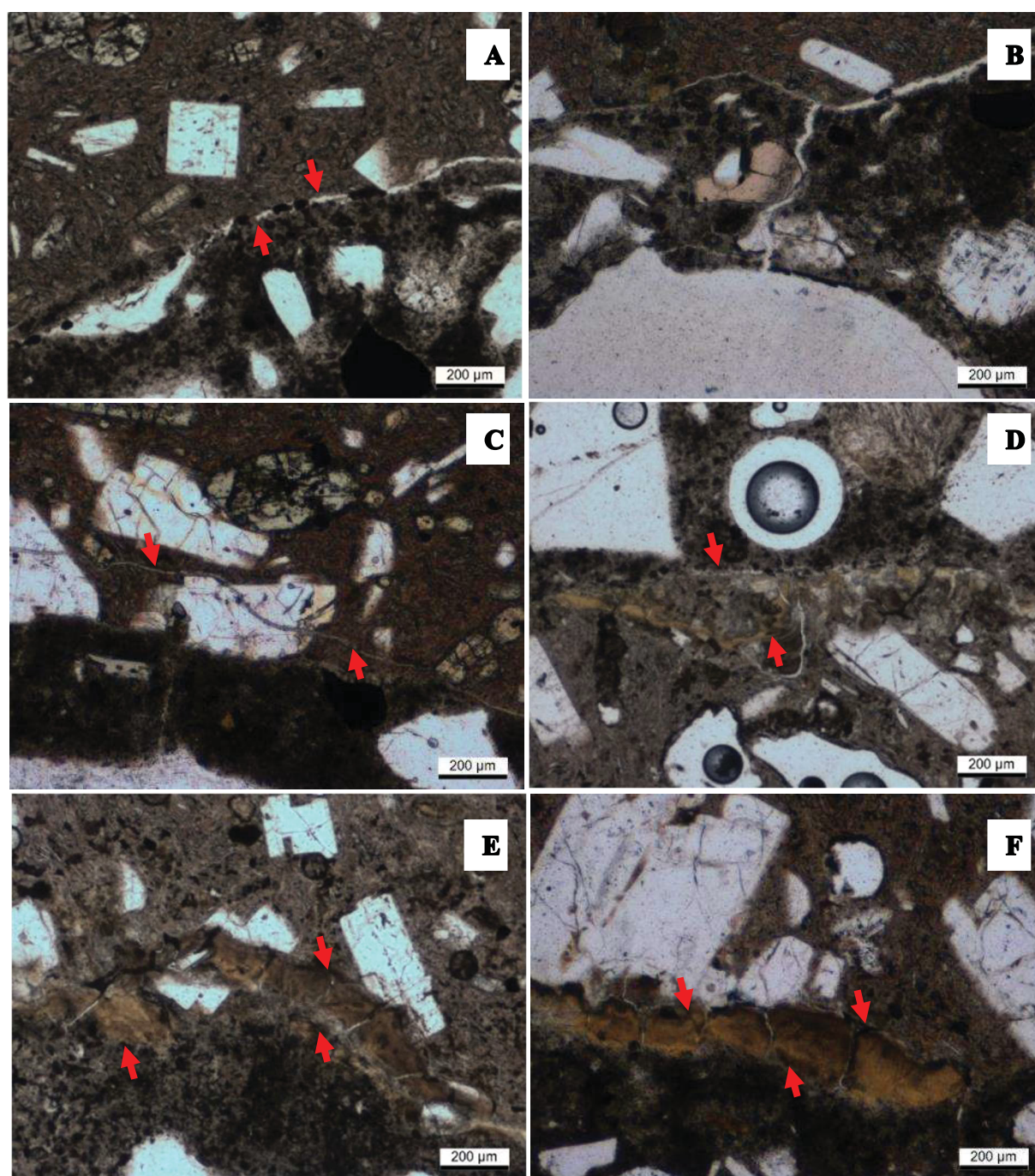


Figure 5.145. Photomicrographs of the TK concrete prism. All photos are in PPL. A) Brownish material in a crack outlining an aggregate particle; B) Cracks in the cement matrix connecting some grains of the sand fraction and a void; C) Cracks within the aggregate particle; D), E) and F) Cracked yellow-brownish material located in different locations of an aggregate particle at the boundary between particle and cement paste.

There is an evidence for an ongoing ASR in the present concrete, where the andesitic aggregate particles are responsible.

CHAPTER 6

ANALYSIS AND DISCUSSION

The results obtained in the present work are discussed in this chapter. Some considerations are given regarding the petrography of the aggregates, rock suites and geological setting; the correlation between the results of laboratory investigations and post-mortem petrography. The data generated are summarized in Table 6.1.

Table 6.1. Results from all the methods used with the different aggregates. The results highlighted in blue indicate the samples classified as reactive in all laboratory expansion tests and by petrography.

Samples	Country	Chemical Classification	Potentially reactive forms of silica identified by petrographic characterization	AMBT expansion, % 14 days	CPT expansion, % 1 year	GPT 19 weeks	DRI post mortem
BRAZ	Brazil	Basalt	Volcanic glass (53-55%), altered volcanic glass, chalcedony, clay minerals (e.g., smectite?)	0.48	-0.01	Gel in some particles	284
CAN	Canada	Basalt	Volcanic glass (52-55%)	0.02	0.01	No gel	-
ICL1	Iceland	Gravel (basalts, metabasalts, dacite, rhyolite) *	Volcanic glass (68%), altered volcanic glass, tridymite, clay minerals (e.g., smectite)	0.44	0.02	Gel in some particles	388
ICL1 fine sand		Sand (B)	1	0.46	0.20	Gel in several sand particles	1417
ICL1 coarse sand		Sand (B)	1	0.34	0.25	Gel in several sand particles	1877
ICL2		Gravel (basalts, metabasalts rhyolites) *	Volcanic glass, altered volcanic glass, tridymite, clay minerals (e.g., smectite)	0.05	0.01	Gel in some particles	-
ICL3		Basalt (B)	Volcanic glass	0.10	0.01		-
ICL3sand		Basalt (B)	1	0.13	-0.01	Gel in some coarse particle	-
ICL4		Gravel (basalts, dacite, gabbro?) *	Volcanic glass (47-49%), altered volcanic glass, microcrystalline quartz, clay minerals (e.g., smectite)	0.57	0.13	Gel in some particles	620
ICL4 sand		Sand (B)	1	0.63	0.34	Several in sand fraction	2125
JAP	Japan	Andesite	Tridymite	0.79	0.24	Gel in many particles	1208
MOZ	Mozambique	Rhyolite	Volcanic glass (64-71%), tridymite	0.22	0.00	Gel in many particles	37
NZ1	New Zealand	Basanite	Volcanic glass (52-53%), clay minerals	0.01	0.01	No gel	-

Samples	Country	Chemical Classification	Potentially reactive forms of silica identified by petrographic characterization	AMBT expansion, % 14 days	CPT expansion, % 1 year	GPT 19 weeks	DRI post mortem
NZ2		Basalt	-	0.04	0.02	Gel is rare	21
NZ3		Basalt	Volcanic glass (53-71%)	0.58	0.03		67
NOR	Norway	Basalt	-	0.07	0.00	No gel	-
SMA-SM1	Portugal (Azores Islands)	Basanite	-	0.02	0.02	-	238
SMA-SM2		Basanite	-	0.01	0.02	-	210
SMG-SM1		Potassic trachybasalt	Volcanic glass (58%) ²	0.02	0.02	-	114
SMG-SM2			-	0.02	0.04	-	86
SMG-SM3		Basalt	-	0.02	0.02	-	74
TER-SM1		Trachyte	Volcanic glass Micro-crystalline to silica	0.13	0.02	-	203
TER-SM2		Basalt	Volcanic glass (55%) ²	0.02	0.03	-	219
GRA-SM1		Hawaiite		0.01	0.03	-	235
SJO-SM1		Basalt		0.01	0.03	-	49
PIC-SM1		Basalt		0.00	0.03	-	94
FAI-SM1		Hawaiite		0.01	0.02	-	149
FLO-SM1		Benmoreite		0.01	0.01	-	1039
FLO-SM2		Mugearite		0.01	0.01	-	240
CRV		Hawaiite	-	0.02	0.01	No gel	-
CANY1	Spain (Canary Islands)	Basanite	Volcanic glass (44-50%)	0.01	0.01	Gel in some particles	225
CANY2		Basanite	Rare volcanic glass	0.02	0.02		-
TK	Turkey	Andesite	Volcanic glass (71-73%)	0.98	0.14	Gel in many particles	903
HW1	USA (Hawaiian Islands)	Basalt	Volcanic glass (79-80%)	0.77	0.02	Gel in several particles	-
HW2		Basalt	Volcanic glass	0.07	0.01	Gel in some particles	-
HW3		Basalt	Volcanic glass (62-64%)	0.82	0.03	Gel in many particles	178
HW4		Mugearite	Volcanic glass	0.03	0.02	Gel in some particles	59
HW4sand		*	1	0.02	0.01	Gel in several sand particles	-
HW5/6		Basalt	Volcanic glass (77-80%)	0.45	0.02	Gel in several particles	114
HW7		Basalt	Volcanic glass (62-80%)	0.90	0.01	Gel in several particles	112

Samples	Country	Chemical Classification	Potentially reactive forms of silica identified by petrographic characterization	AMBT expansion, % 14 days	CPT expansion, % 1 year	GPT 19 weeks	DRI post mortem
HW7 sand	USA (Hawaiian Islands)	Basalt	1	0.50	0.32	Gel in several sand particles	3373
HW7 CA+FA		Basalt	Volcanic glass	-	0.01	Gel in some particles	194
Spratt	Control agg.	Siliceous Limestone	1	0.39	0.17	Gel in many particles	1270
GBS sand		Sand (B)	1	0.30	0.05	Gel in several sand particles	449
B: mostly basaltic in composition; * no geochemical analysis; ¹ No petrographic analysis was done; ² taken from Medeiros et al. (2012)							

6.1. Petrography of the aggregates, rock suites and geological setting

The results of the chemical analysis plotted in the TAS diagram showed that almost half of the samples analysed in this study are classified as basalts in a restricted sense (TER-SM2, SJO-SM1, PIC-SM1, HW1, HW2, HW3, HW5, HW6, HW7, ICL3, NZ2, NZ3, BRAZ, CAN and NOR) while the rest range between ultrabasic to acid rocks. The latter include basanite (SMA-SM1, SMA-SM2, CANY1, CANY2 and NZ1), hawaiite (GRA-SM1, FAI-SM1 and CRV), potassic trachybasalt (SMG-SM1 and SMG-SM2), mugearite (FLO-SM2 and HW4), benmoreite (FLO-SM1), trachyte (TER-SM1), andesite (JAP and TK) and rhyolite (MOZ). Due to their heterogeneity, the gravel samples from Iceland were only classified based on the mineralogy and texture observed under the polarizing microscope and not with the aid of geochemical analysis, as the other samples. From the point of view of petrography, basalts with different degrees of alteration (some are metabasalts), glassy basalt, dacite, rhyolite and a coarse-grained rock similar to gabbro were identified. It is noticed that the islands have more variety of volcanic rocks ranging from basanite to rhyolite than the ones from continental regions.

The petrographic study of the different aggregates showed similarities but also distinct features and mineralogy among some of them, even between basalts. In general, the basalt samples contain similar mineralogy with phenocrysts and microphenocrysts of plagioclase, usually clinopyroxene and less commonly orthopyroxene (only present in the HW5, HW6 of the tholeiitic suite), with or without olivine. The opaque minerals occur as accessory minerals in the form of titanomagnetite and ilmenite. The groundmass has the same mineral

assemblage with or without volcanic glass, apatite and sometimes with biotite. Also, they present the same type of textures, intergranular to intersertal, glomeroporphyritic, subophitic and sometimes variolitic.

The NOR and CAN aggregates are the most distinct amongst the basalts studied. Both samples have chlorite and calcite that are either replacing other minerals (e.g. plagioclases) or filling vesicles (amygdales) in the rock. In addition, silica minerals and epidote minerals are present in the NOR sample and may be present in the CAN sample according to Lebel and Hubert (1995), although they were not identified in the present samples by petrography. Regarding the NOR sample, part is published in Norwegian by Berg (1985) who describes the mineralogy and the pseudomorphs associated. The only difference between the two samples is that volcanic glass was only identified in the CAN aggregate. In the NOR sample, probably volcanic glass has already been altered into different minerals. The presence of certain minerals in these two basalt samples indicates that both rocks have been suffering alteration with time. Epidote is commonly produced during the alteration of plagioclase (Cox et al., 1979) and volcanic glass (Gifkins et al., 2005); calcite is a common mineral of secondary mineralization (Deer et al., 2013) and is also an alteration product of plagioclase, volcanic glass and ferromagnesian minerals (Gifkins et al., 2005); chlorite is usually found: filling amygdales in lavas associated with epidote, alkali feldspar, quartz and carbonates, among others; replacing iron rich ferromagnesian minerals (Deer et al., 2013); and replacing plagioclase and volcanic glass (Gifkins et al., 2005). The CAN and NOR samples, besides their common mineralogy, have other aspects in common, namely, they belong to the alkaline series and they are the products of a continental rift in accordance to Nilsen (1992), La Flèche et al. (1993) and Hodych and Cox (2007); they are old rocks, NOR sample is from Palaeozoic age and CAN sample is from Neo-Proterozoic age.

Other distinct features were observed in basalts from the Icelandic gravels. According to Sveinsdóttir and Wigum (2003), the aggregates in Iceland come from fluvial-, glaciofluvial and sea-dredged deposits (mostly from erosion of lava beds, pillow lavas and pillow lava fragments), as well as crushed rocks. Helgasson (1990) affirms that the bedrock of Iceland is mainly formed by basalts and there is less than 10% of sediments and plutonic rocks. The same author state that most Icelandic aggregates are exploited from gravel pits and that the most common rocks found in the Icelandic aggregates are basalt, glassy basalt, clastic rock, hyaloclastite and rhyolite; shell fragments are also present. The gravels form a mix of rock fragments where basalt represents the major component with different degrees of alteration that includes in some cases metabasalt. Dacite and rhyolite represent the rest of the gravel fragments where shell fragments are also present. According to Bucher and Grapes (2011),

the metamorphic derivatives of basic rocks (45-52 wt.%) are known as metabasic or metabasaltic rocks. The fragments of metabasalt in the gravels are those with the most peculiar features where the pore spaces are filled with zeolites and chlorites. This type of feature is similar to what is described by Neuhoﬀ et al. (1999); they describe the mineral paragenesis in the different stages of alteration observed in basaltic lavas aﬀected by near-surface alteration, burial metamorphism and hydrothermal alteration in Eastern Iceland. The metabasalt found in ICL1 and ICL2 samples is in accordance with stage II referred by the same authors. Chlorite forms mixed layers with smectite (C/S) either in the groundmass or in the rims of the pores, zeolite fills the centre of the vesicles and plagioclase is being replaced by zeolite. All these minerals have been confirmed by petrography and EMPA in the present work. According to the authors above, the formation of C/S in the groundmass is due to the alteration of olivine and basaltic glass and that the increase of the infilling of C/S in the vesicles is due to the rise of temperature with time as the lavas are being buried; on the other hand, the zeolite assemblage (scolecite or heulandite, stilbite, mordenite, epistilbite) appear at the end of stage II, after burial, being indicative of the regional metamorphic zone of low-grade metamorphism. Volcanic and altered volcanic glasses are also present in the basaltic aggregates being discussed further in this section.

The basalt from BRAZ also displays some distinct mineralogy. In some aggregate particles, quartz or a silica polymorph was identified as associated with radiated green celadonite (a mineral that belongs to the mica group). The EPMA analyses showed SiO₂ values of 90%. Although it was previously suspected to correspond to opal (Medeiros et al., 2021), the petrographic properties indicate that it could be quartz. Brown clay minerals scattered in the groundmass were identified, whilst only grains of quartz and chalcedony are present in other particles. According to Nicola (1994), who studied the pedological systems developed on basalts from Ilha Solteira, this basalt contains, among other minerals, dykes of fibrous silica (possibly chalcedony) and 9% of secondary green phyllosilicates that could correspond to the celadonite identified earlier in chapter 5.

The basanite from New Zealand (NZ1) also showed some different minerals and mineraloids. The petrography identified chlorite and zeolites in the interstices of the rock, zeolites filling vesicles together with calcite and a small amount of what might be palagonite, a material similar to what was observed in Iceland samples. The zeolites in the groundmass were confirmed by EPMA. According to Graham et al. (2003), this basanite contains different assemblages of zeolites and usually interpenetrating crystals and inclusions of vermicular pale emerald-green chlorite.

Besides basalt, other rock types were observed and studied such as rhyolite, andesite, trachyte, dacite and a coarse-grained aggregate similar to gabbro.

The rhyolites from Iceland (ICL1, ICL2, ICL4 and GBS) and Mozambique (MOZ) are very similar; all are aphyric with darker and lighter areas. They are formed by the devitrified volcanic glass and mainly quartz, feldspar and tridymite. Helgasson (1990) affirms that rhyolite is one of the rocks considered potentially reactive in Iceland.

The study of andesite in the present work was mainly used for comparative purposes since its reactivity to alkalis has already been proven. The two andesite samples (JAP and TK samples) have in common the porphyritic texture with the presence of plagioclase, clinopyroxene and orthopyroxene phenocrysts and they belong to the calc-alkaline suite. The difference between the two samples is mainly related to the groundmass composition. The JAP groundmass contains tridymite with no visible glass while the groundmass of the TK sample is mainly formed by volcanic glass. These contain silica polymorphs and rhyolitic volcanic glass, all classified as highly reactive from the point of view of ASR. In the case of JAP sample, it can contain volcanic glass and cristobalite, or tridymite depending on the zone that it was taken from the quarry according to the researcher Dr. Yamada (personal communication). The andesite from JAP was described by Yamada et al. (2014) while the TK sample was reported by Çopuroglu et al. (2009) and Fernandes and Andiç-çakır (2015).

The trachyte from Azores Archipelago is another different rock that was previously studied by Medeiros (2011) who identified the presence of microcrystalline quartz in the groundmass, confirmed by SEM/EDS, and rare volcanic glass in the groundmass.

Also, some distinct rock particles were observed in the gravels from Iceland, a coarse-grained aggregate particle that looks like gabbro, an aggregate particle that seems to have suffered hydrothermal alteration and dacite. The first two were identified only in the ICL4 sample. Dacite occurs in ICL1 and ICL4, showing a spherulitic texture. Gabbro is a common rock in Iceland according to the Icelandic Institute of Natural History, it occurs as intrusive bodies (Thorarinsson and Tegner, 2009) or as xenoliths in lavas (Gurenko and Sobolev, 2006). The aggregate particle that seems to be hydrothermally altered contains pyrite, calcite and silica minerals. Pyrite was confirmed by EDS analysis. The rock is altered and phenocrysts of plagioclase are being replaced by other minerals. According to Steinþórsson (2005), the dacites together with rhyolite are almost exclusive from Iceland compared to other Islands. The presence of several spherules in the rock points to the devitrification of glass. According to Helgasson (1990), dacite is one of the rocks that is considered reactive in Iceland. The volcanic glass present in ICL1 dacite contains an average SiO₂ content of 72% (obtained in EPMA).

Volcanic glass was identified in several of the samples studied. In the islands, all samples from the Hawaiian Islands and Iceland contain volcanic glass while it was identified only in three of fourteen samples studied from the Azores archipelago (SMG-SM1, TER-SM1 and TER-SM2 samples); however, in the post-mortem petrography of the concrete prisms, volcanic glass is present in some aggregate particles, especially in the case of FLO-SM2. It was identified in two of three samples from New Zealand (NZ1 and NZ3 samples) and in one of two samples from the Canary Islands (CANY1). Regarding the continental regions, glass was found in all samples except for the NOR sample. Volcanic glass shows distinct features, composition and colours in the several samples analysed, which is influenced both by the composition of the magma and its viscosity. For example, in part of the Hawaiian samples, volcanic glass seemed to be filling the vesicles of the rock, associated with needles of apatite. This was also reported by Chapman (1947) who describes the presence of vesicular basaltic glass with tiny needles of apatite and minute particles of iron ore in the lavas from Kilauea. In the Icelandic samples, the volcanic glass occurs as sideromelane and palagonite. The sideromelane is homogeneous yellow-beige under PPL and isotropic in XPL, while palagonite is heterogeneous with a brown-gold-orange colour under PPL and isotropic to anisotropic with a fibrous habit under XPL. Helgasson (1990) describes that the basaltic aggregates contain glass in the groundmass and some are beginning to show alteration; there is a rim of palagonite in the basaltic glass. In the BRAZ sample, the glass appears in green and in light brown colours, filling the interstices of the basalt. There is another greenish but anisotropic material that is scattered all over the rock that could be chlorophaeite, which is considered a mixture of Fe-montmorillonite and Fe-saponite according to Środoń et al. (2019) and an amorphous hydrated Fe-Mg silicate in accordance with Meyer (1978). The results of EPMA showed a high amount of iron ($> 20\%$), which is consistent with other results obtained for chlorophaeite (Peacock and Fuller, 1928; Peacock, 1930; Środoń et al., 2019). However, it could also be palagonite with the same iron content as shown in Stroncik and Schmincke (2002), although the iron values for palagonite are frequently below 20%. Chlorophaeite is commonly mentioned in Brazil as a reactive component of basalt (Hasparyk, 1999; Munhoz and Cincotto, 2008; Couto, 2008; NBR 15577-3, 2018) and also palagonite (Hasparyk, 1999; Couto, 2008); both are considered potentially reactive to alkalis.

Another interesting point related to volcanic glass is the chemical composition obtained for the different samples through EPMA. It is important to emphasize that according to Katayama et al., (1989), rhyolitic volcanic glass ($\text{SiO}_2 > 70\%$) is considered highly reactive while glass containing 52% (basaltic glass) of SiO_2 lacks of reactivity; also, the same authors affirm that fresh volcanic glass with SiO_2 content $> 65\%$ (dacitic glass) is considered reactive. The results

from EPMA showed that the basanite of CANY1 and the basalts of ICL1 and ICL4 have SiO₂ contents lower than 50%, while the rest of the samples where the analysis of the volcanic glass was performed have higher SiO₂ content ranging from andesitic to rhyolitic glass. The Hawaiian samples are the ones with the highest values ranging from dacitic to rhyolitic glasses with average SiO₂ values ranging between 62% (HW3) and 80% (HW1). It seems that the Hawaiian samples are considered highly reactive except for HW3 in accordance to Katayama et al. (1989). The other two highest values are related to the analysis of the volcanic glass from TK and MOZ samples. The volcanic glass obtained for the TK sample is consistent with that reported in Fernandes and Andıç-çakır (2015) with an average of 72% of SiO₂, being considered alkali reactive. The values obtained for the MOZ sample show an average of 67% SiO₂, a glass of dacitic composition that can be considered highly reactive. Also, the composition of a volcanic glass of the NZ3 basalt shows an average of 64% of SiO₂, a glass of andesitic composition that does not seem to be reactive in accordance to Katayama et al. (1989).

The relation between volcanic rocks, their rock suites and the tectonic settings has shown some distinct petrographic characteristics in the volcanic rocks. The differences are mainly related to the chemical composition of the minerals, the abundance or not of certain minerals and the presence of volcanic glass. In accordance to Wilson (1989), the tholeiitic series occurs in all tectonic settings (MORB, Continental rift, Island arcs, Ocean islands and Large Igneous Provinces) and commonly contains Ca-rich (augite) and Ca-poor pyroxene (hypersthene), rare olivine and concentration of Fe-Ti oxides in the groundmass of basic rocks. The calc-alkaline rock series is usually applied to island arcs or subduction zone rocks ranging from basalt to rhyolite or a magma series intermediate between the low-K and high-K series or andesite (Sheth et al., 2002). In the island arcs, the rocks range from basalt to rhyodacite with an anhydrous phenocryst assemblage of plagioclase, olivine, clinopyroxene, orthopyroxene, magnetite, and rare ilmenite. The alkaline series is also present in different tectonic settings such as continental rifts, island arcs, ocean islands and large igneous provinces (Wilson, 1989).

The separation between alkaline and tholeiitic/subalkaline series is given by the TAS diagram after Le Bas et al. (1986) but is also obtained based on the concept of Yoder and Tilley (1962) with the use of normative minerals. Despite how it is obtained, in the studied rocks the ones that belong to the tholeiitic series have higher SiO₂ content than those belonging to the alkaline suite. This is the case for the majority of the Hawaiian (HW1, HW2, HW3, HW5, HW6 and HW7) and New Zealand (NZ2 and NZ3) samples and also for Brazil (BRAZ) sample. Frost and Frost (2014) consider that Hawaii is a little unusual when compared to other oceanic

islands because it has a large volume of tholeiitic rocks and a small volume of alkaline rocks while for example Azores have a larger proportion of alkaline rocks. Also, and according to Mackenzie et al. (1982), tholeiitic basalts contain more interstitial volcanic glass than the ones from the alkaline suite, which is considered to be rare. However, there are some exceptions in the rocks from the alkaline suite like CANY1, HW4 and NZ1, which contain some volcanic glass, the latter showing a high quantity of interstitial volcanic glass with an intersertal texture. Also, Irvine and Baragar (1971) state that for the rocks that belong to the tholeiitic and the calc-alkaline series, the groundmass commonly contains interstitial quartz (or other silica minerals, or silica-rich glass). According to Cox et al. (1979), certain volcanic rocks of the calc-alkaline suite from island arcs, like the two pyroxenes andesite, can contain interstitial silica minerals of late crystallization that include mainly tridymite and cristobalite. All these are in accordance with what was obtained for the JAP, MOZ and TK samples that belong to the calc-alkaline suite. Tridymite was identified in the JAP and MOZ samples, while the interstitial volcanic glass in the TK sample is rich in silica with an average SiO_2 content of 72%.

The calc-alkaline rock series is restricted to subduction-related tectonic settings in accordance to Wilson (1981). However, Sheth et al. (2002) state that it should not have a tectonic connotation. The referenced authors criticize the use of tholeiitic and calc-alkaline series saying that the IUGS Subcommittee on Systematics of Igneous Rocks (Le Bas et al., 1986) has eliminated both the terms “calcalkaline” and “tholeiite,” and seemingly replaced the two rocks suites by “subalkaline”. The authors further discuss that the TAS diagram and the AFM diagram are not suitable to identify the calc-alkaline series saying that there are appropriate geochemical variation diagrams. They also affirm that even when the calc-alkaline suite of rocks is identified with the right criteria it should not have a tectonic connotation. In despite of using or not the calc-alkaline and the tholeiitic terms, the results obtained showed that the SiO_2 content is higher in the rocks situated in the subalkaline series of the TAS diagram and that they usually contain more volcanic glass than those belonging to the alkaline series. The calc-alkaline series usually have tridymite and/or cristobalite in the groundmass.

Regarding the normative minerals, Irvine and Baragar (1971) affirm that the rocks of the tholeiitic basalt and calc-alkaline series usually show orthopyroxene in the norm and may have quartz, while most rocks in the alkali olivine basalt series have nepheline. This is consistent with the rocks studied. Also, Yoder and Tilley (1962) divided the basalts into five groups according to their normative components; from the five groups, it is important to mention the group of the oversaturated tholeiites with normative quartz and hypersthene, the group of the olivine tholeiite (undersaturated) with normative hypersthene and olivine and the group of alkali basalt with normative olivine and nepheline. From the studied rocks, the ones that are more

interesting from the point of view of alkali-silica reactivity are those oversaturated in silica, like HW3, HW5, HW6 and HW7 samples. According to Katayama et al. (1996), volcanic rocks oversaturated in silica often contain cristobalite and tridymite which are considered reactive minerals. For Iceland, it was not possible to obtain this result due to the heterogeneity of the gravels, but according to Helgasson (1990), the majority of the aggregates used in Iceland belong to the tholeiitic basalt series.

6.2. Correlation between the results of laboratory investigations

As indicated in Table 6.1, the highest CPT expansions were obtained in this study for specimens incorporating reactive or potentially reactive sands, i.e. specimens ICL1 coarse sand, ICL1 fine sand, ICL4 sand, HW4sand, HW7sand. Significant concrete prism expansions were also obtained in the case of the specimens incorporating coarse aggregates ICL4, JAP, TK and Spratt (control). However, significant differences are observed regarding the potential reactivity of the aggregates selected for this study when determined according to the AMBT and the CPT. The number of aggregates considered potentially reactive is higher in the AMBT than in the CPT. This is well illustrated in figure 6.1, which correlates the one-year CPT and 14 – day AMBT expansions for all tested samples. The graph also includes the expansion limit for the CPT, which is 0.040% at one year in the vertical line, and the expansion limit for AMBT, which is 0.10% for 14 days in the horizontal line. The graph shows four zones – I, II, III and IV. Most of the samples fall in zone I (57%) where they are classified as innocuous in both tests. The ones that fall in zone II (23%) suffered from excessive expansion in the AMBT creating a “false-positive” result but they are not considered reactive according to the limit established for the CPT test. The samples in zone III (20%) were classified as potentially reactive (reactive in the case of the CPT) in both test methods. No samples fall in zone IV where they would be classified as potentially reactive in the CPT but innocuous in the AMBT. In general, both the CPT and AMBT agree in 77% of the cases (results falling in zones I and III) evaluated in this study for the potential alkali-reactivity of aggregates.

Thomas et al. (2013a) and Robertson and Shen (2018) also studied aggregate specimens collected from sources HW1, HW4 and HW5/6, where all were considered reactive by the AMBT. Robertson and Shen (2018) concluded that those results could be considered false positives and that the AMBT was not reliable for the evaluation of the potential for ASR (at least with those types of aggregates) and should not be used as the only indicator of the potential for ASR. However, the authors did not perform a petrography study of the samples

to verify if there was a correlation between the results of the laboratory tests and the composition of the samples.

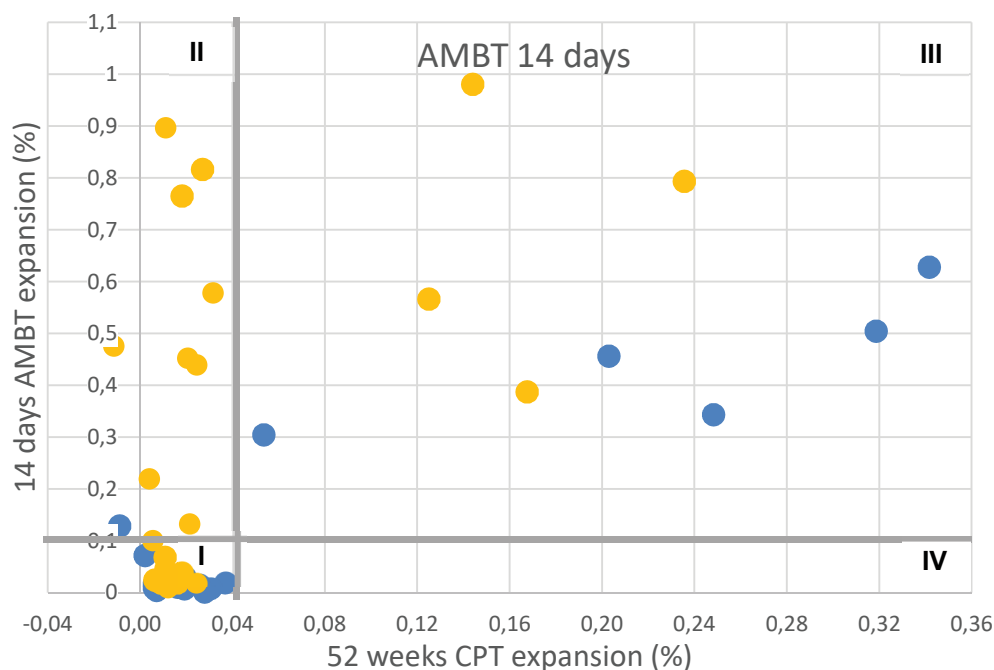


Figure 6.1. Correlation between CPT and AMBT results. The yellow dot colour represents all the samples that contain volcanic glass. The grey vertical line represents the limit of 0.04% expansion for the CPT test and the grey horizontal line the limit of 0.10% for the AMBT.

As can be seen in Table 6.1, all basaltic rocks that showed potential reactivity according to the AMBT contain volcanic glass; on the other hand, not all the basaltic rocks with volcanic glass were systematically considered potentially reactive in the AMBT. The petrographic examination of all aggregate specimens indicates that most of the specimens incorporating glass have suffered from significant expansion obtained in the AMBT. The samples being considered potentially reactive in the AMBT are HW1, HW3, HW5/6, HW7, HW7 sand, ICL1, ICL1 fine sand, ICL1 coarse sand, ICL3, ICL3 sand, ICL4, ICL4 sand, JAP, NZ3, BRAZ, MOZ and TK. Also, an increase in AMBT expansion somewhat corresponds to specimens with a volcanic glass of higher SiO_2 composition (Figure 6.2A), which is however not the case for expansion in the CPT (Figures 6.2B).

Several researchers concluded that the presence of volcanic glass in basalts enhances the expansion of AMBT. Korkanç and Tuğrul (2005) studied some basalts from Turkey where the presence of volcanic glass with acidic-intermediate character showed AMBT expansions higher than 0.10%. Marfil et al (2013) and Madsen et al. (2019) reported that when volcanic

glass and clay minerals are present, they are associated with high accelerated mortar bar expansions. One of the hypotheses to explain the peculiar behaviour observed in the AMBT for several basaltic aggregates is that the high temperature to which the mortar bars are subjected (80°C) likely affects the volcanic glass present in those aggregates and turns it into deleterious and expansive. Pedersen et al. (2016) reported that the exposure temperature and/or exposure of samples to a large alkali supply in the AMBT might have different effects on several rock types and particle sizes.

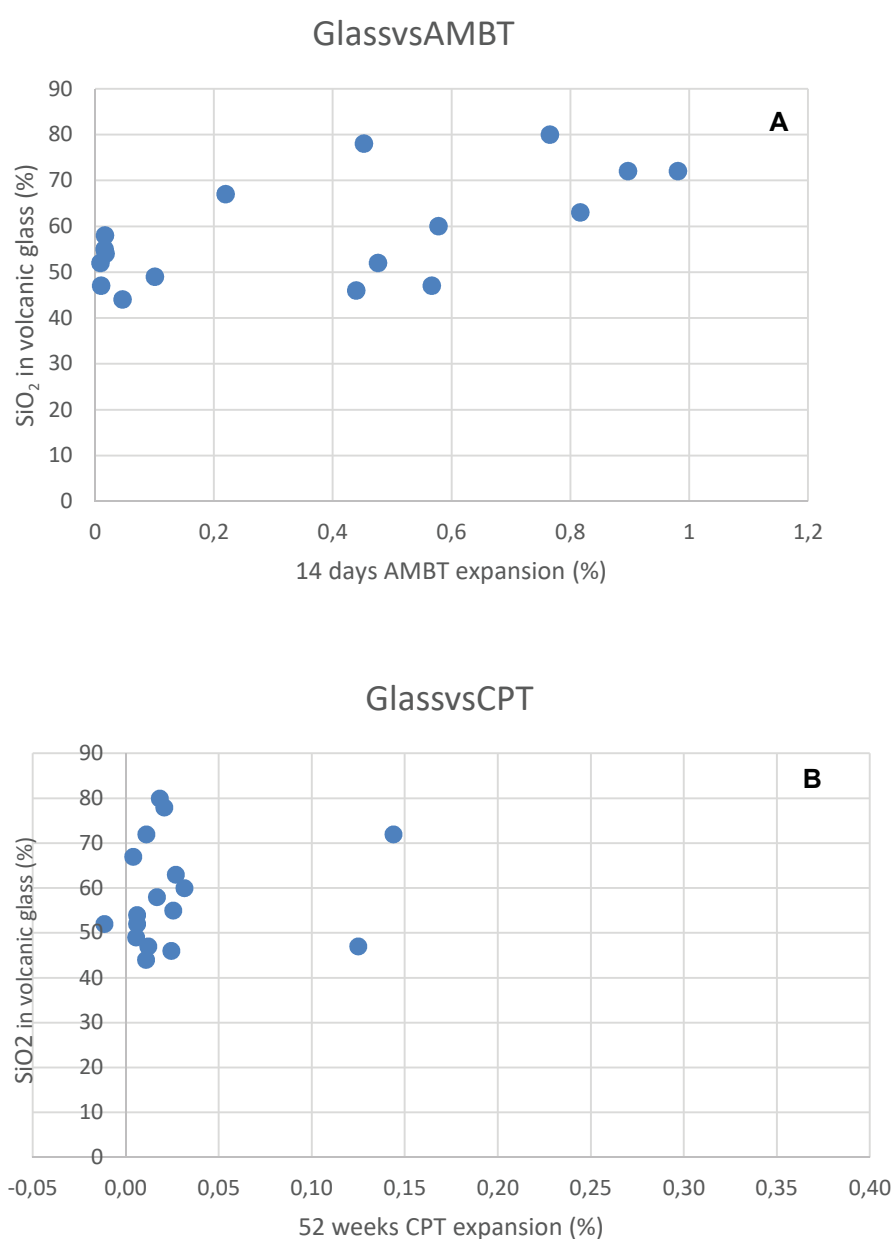


Figure 6.2. Correlation between the SiO₂ composition of volcanic glass and expansion tests: A) Glass composition vs AMBT and B) Glass composition vs CPT.

Regarding the CPT, the highest expansions were obtained for the samples that used volcanic sand as fine aggregates. There is indeed a clear dominance of the reactivity on the sand fractions rather than in the coarse aggregate fractions in the samples from Iceland (ICL1 fine sand, ICL1 coarse sand and ICL4 sand) and in one from Hawaii (HW7 sand). Wigum (2012) also showed high CPT expansion for a mixture composed of 100% of reactive sand from Iceland and a non-reactive coarse aggregate from Norway (RILEM AAR3 and RILEM AAR4.1). On the other hand, he also reported opposite results for the same materials when investigated through blocks stored in an outdoor field exposure site. Based on those results, the author recommended that more tests be conducted to know if this effect is only due to the aggregate grain sizes or to some pessimum behaviour of aggregates. In another exposure site located at the University of Hawaii, in Manoa, 30 concrete blocks were cast from various concrete mixtures (with and without SCMs and lithium-based admixtures) all incorporating local basaltic aggregates. Only one of the mixtures incorporating basaltic rock used both as coarse and fine aggregates showed signs of ASR expansion and cracking in the field study and also an expansion in the CPT and in the AMBT (Thomas et al 2013a; Robertson and Shen, 2018). According to Robertson and Shen (2018), this aggregate is currently not used for concrete manufacture, and it was recommended that it should be used only with validated mitigation measures.

Results from expansion testing in the literature have shown that very fine fractions of “reactive material” do not cause excessive expansion but rather a pozzolanic reaction (Poyet et al., 2007; Pedersen, 2016). According to French (1994), the most damaging size range appears to be of 3-7 mm for rapid reactive rock types such as chert and volcanic glass. Zang et al. (1999) also showed that for siliceous aggregates, the smaller the size (0.15-10mm) the greater the expansion while coarser sizes caused less expansion in an autoclave test. Pedersen et al. (2016) referred to the work of Nishibayashi and Yamura (1992) where the authors used reactive andesite for CPT at 40°C. They verified that the expansion of the test specimens incorporating reactive fine aggregates increased rapidly whereas that of the specimens made with coarser fractions reacted more slowly in the beginning but continued to expand for longer periods.

Regarding the pessimum proportion, Katayama (1997) and Katayama et al. (2021) showed that rhyolitic glass has a pessimum proportion of 100%. Katayama et al. (2021) reported that the pessimum proportion of volcanic rocks depends on the cooling rate of the magma, ranging from 10% (cristobalite) to 100% (glass). Binal (2015) concluded that the reactivity of an andesite aggregate was due to the presence of interstitial volcanic glass and that in the case

of highly reactive andesite aggregate used in concrete mixtures, a pessimum behaviour can be observed (80%).

Also, another interesting fact is that the Mozambique rhyolite sample (MOZ) was considered non-reactive in the CPT, despite of including volcanic glass with an average SiO_2 content of 67% and the presence of tridymite. It is interesting to note that the MOZ aggregate showed somewhat lower 14-day AMBT expansion (0.22%) than expected; however, this could be potentially attributed to the higher porosity of that material.

6.3. Post mortem petrography and gel formation

The petrographic examination conducted at the completion of the accelerated mortar bar and the concrete prism tests revealed a much larger quantity of visible signs of deterioration in the thin sections of the mortar bars than in those made from concrete prisms. These signs of deterioration included microcracks filled with gel in the aggregate particles and in the cement paste, the possibility of identifying the reactive aggregates and reaction rims. This seems to be directly related to the results obtained in the AMBT, where more aggregates induced higher AMBT expansions and were then considered potentially reactive when compared to the CPT. Even so, the petrographic examination of concrete prisms incorporating aggregates considered reactive revealed relatively less deterioration when compared to that observed in the AMBT specimens. It was indeed noticed less cracks filled with gel and the aggregate (s) that was (were) causing the reaction/expansion were sometimes less easily recognizable in the concrete specimens.

Regarding the DRI results, increasing CPT expansion generally results in higher DRI values. Some aggregates showed a very low DRI value (< 100) with very few cracks in the aggregate particles or in the cement paste and no/rare gel. This was the case for SMG-SM2, SMG-SM3, SJO-SM1, PIC-SM1, HW4, NZ2, NZ3 and MOZ. On the opposite, others showed a very high DRI value (> 1000) with a huge number of cracks in the aggregate particles and in the cement paste either filled with gel or not; these include HW7 sand, ICL1 fine sand, ICL1 coarse sand and ICL4 sand. They are mainly related to the use of volcanic sand as fine aggregate, together with a non-reactive coarse aggregate (HP) in the CPT method (yellow dots in Figure 6.3). However, there are some exceptions: (1) FLO-SM1 has a very high DRI (1417) with several opened cracks but with no gel; and (2) Spratt is a known case of ASR where the reactivity is due to the siliceous limestone coarse aggregate.

With a one-year expansion of about 0.32%, the concrete section incorporating HW7 sand gave the highest DRI value (3373), where almost every 1 cm^2 square showed several cracks in the cement paste filled with gel. On the other hand, a DRI value of only 112 was obtained

for the HW7 specimen made with the coarse aggregate from the same quarry, with limited cracking identified in the test specimen; this correlated well with the corresponding low one-year CPT expansion of 0.011%. The petrographic examination did not show any differences in petrographic characteristics between HW7 and HW7sand. Interestingly, when the coarse and fine aggregates from the HW7 source were used together, a DRI of 194 was obtained, which also correlated with the low one-year CPT expansion of 0.014%. It is difficult to know whether the somewhat peculiar behaviour of the HW7 sand would be observed with other aggregates because not all aggregates investigated in this study were available/tested both as coarse and fine aggregates from the same source. Nevertheless, the GBS sand showed lower values of DRI (449) compared to the results obtained for the mixtures incorporating volcanic sand fractions plus HP coarse aggregate. Zhang et al. (1999) referred to Nishibayashi and Yamura's research that showed that in specimens containing both reactive coarse and fine aggregates from the same source, the expansion is rather small and becomes constant in the early stage.

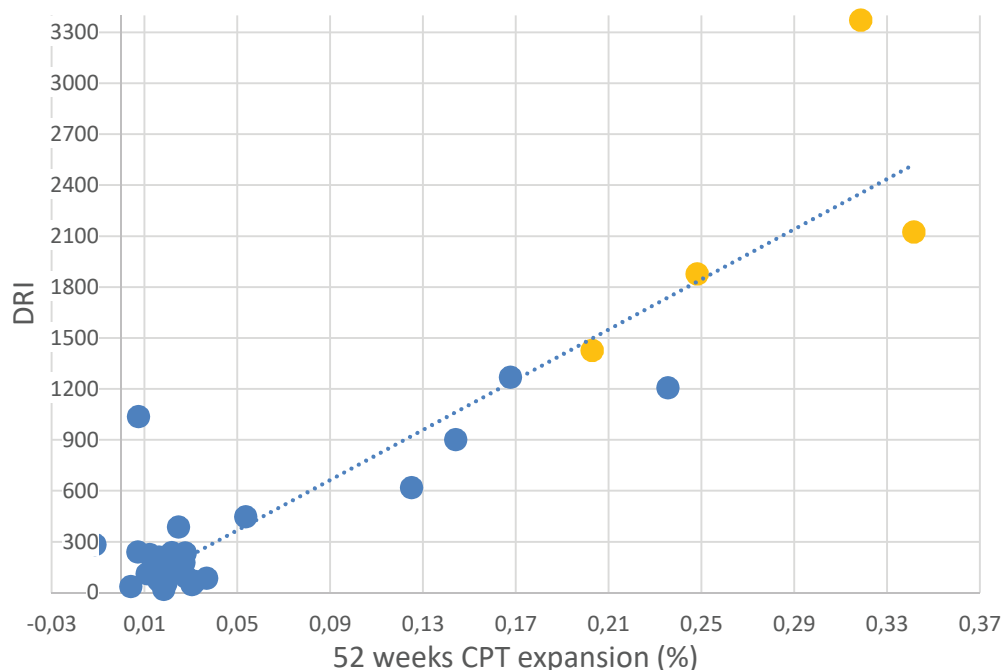


Figure 6.3. Correlation between one-year CPT expansion and DRI results. Yellow dots correspond to the test specimens incorporating volcanic sand fractions.

There is no obvious correlation between the results of the DRI and the rating given to gel formation obtained in the GPT (Tables 5.26 and 5.43). This is illustrated in Figure 6.4. On the other hand, a better correlation is obtained between gel formation and the results of the DRI

when focusing on aggregates containing volcanic sand as fine aggregate, which have several particles with gel (Table 6.2).

Table 6.2. Comparison of the results obtained in DRI for sand aggregates and GPT.

Sample	DRI	GPT Observation
HW7 sand	3373 - Severe to very severe - Concrete with severe signs of deterioration	Several in sand
ICL1 fine sand	1417 - Severe to very severe - Concrete with severe signs of deterioration	Several in sand
ICL1 coarse sand	1877 - Severe to very severe - Concrete with severe signs of deterioration	Several in sand
ICL4 sand	2125 - Severe to very severe - Concrete with severe signs of deterioration	Several in sand

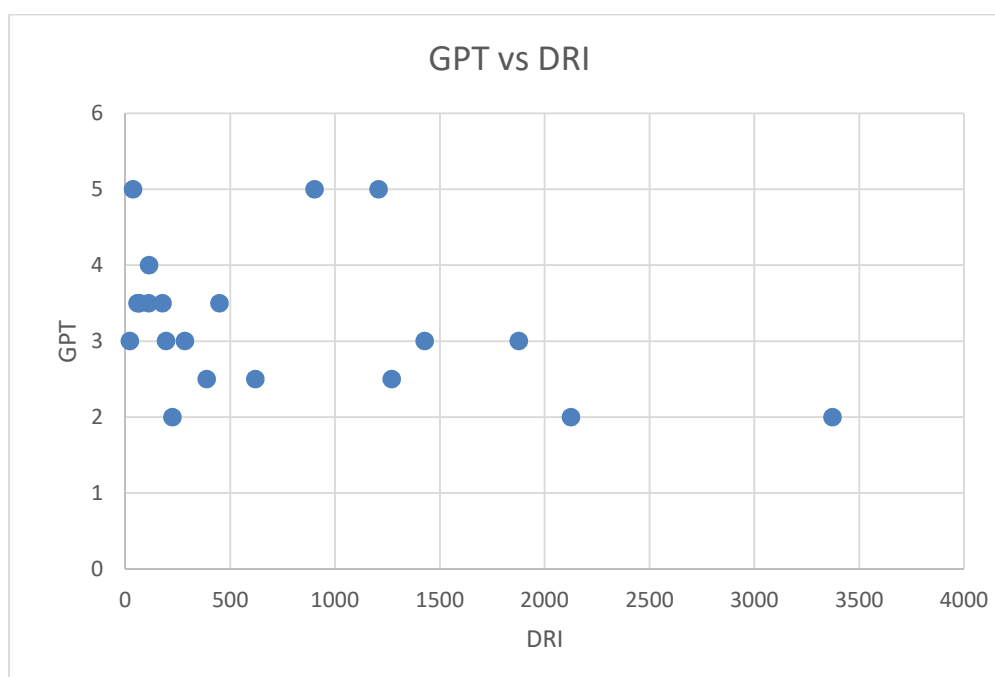


Figure 6.4. Correlation between the gel formation rating obtained in the GPT and the DRI.

CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH

7.1. Conclusions

In this Ph.D. research, several volcanic aggregates from diverse countries and geological settings were subjected to different test methods to characterize their potential reactivity to alkalis when used in concrete. These included aggregates from Brazil (one basalt), Canada (one basalt), Iceland (six mixed sands/gravels, one basalt crushed coarse aggregate and one sand manufactured from basalt rock), Mozambique (one rhyolite), Japan (one andesite), New Zealand (one basanite and two basalts) Norway (one basalt), Portugal - Azores (five trachybasalts, four basalts, two basanites, one trachyandesite, one basaltic trachyandesite and one trachyte), Spain – Canary (two basanites) and United States of America – Hawaiian Islands (five basalts and one basaltic trachyandesite). The above aggregates are mainly of basic composition; two known reactive andesites (from Japan and Turkey) and a siliceous limestone (from Canada) were also analyzed to serve as a reference, especially for laboratory expansion testing.

The following methods were applied to the various aggregates selected:

- Petrographic examination of the aggregates through the use of the polarizing microscope followed by more detailed examinations that comprised: Electron Microprobe analysis (EMPA) with WDS and EDS analysis;
- Geochemical analyses;
- Expansion testing for ASR
 - Accelerated Mortar Bar Test (AMBT) (AAR-02, CSA A23.2-25A or ASTM C 1260);
 - Concrete Prism Test (CPT) (AAR-03, CSA A23.2-14A);
- Post-mortem petrography
 - thin sections of mortar bars and concrete prisms at the completion of the above expansion test;
 - Damage Rating Index on polished prisms at the completion of the CPT (in accordance with the procedure proposed by Villeneuve et al., 2012); and
- Gel formation by the aggregates in an alkaline solution through the use of the Gel Pat Test (inspired by the method used by Fournier and Bérubé, 1993).

One of the main purposes of this work was to determine whether basalts s.l. should be considered potentially reactive or not from the point of view of alkali-silica reaction (ASR) and if so, what is the source of that reactivity. Argentina is one of the countries where basalts are considered/reported as potentially reactive in field concrete structures due to the presence of volcanic glass, fresh or altered, clay minerals and silica minerals. The reported cases show that local coarse basalt aggregate when used together with siliceous sand generates gel,

cracks and reaction rims. On the other hand, Brazilian concrete structures do not seem to show the same problems as ASR due to the use of basalt. When ASR is present, the damage is very limited or the reaction stopped and reached some degree of stabilization without showing any significant deterioration. Iceland is another country where different studies related concrete deterioration not only to the presence of rhyolitic rocks but also to altered basalts associated with unwashed sea-dredged material. Researchers from the two last countries emphasize the severe climatic conditions that accelerate concrete deterioration. In addition, in Azores Archipelago (Portugal), the concrete deterioration of an airport pavement with basaltic aggregates (basanites) seem to be related to the climatic conditions where sometimes the seawater carried by the rain and the wind favours the deterioration, together with the presence of clay minerals and zeolites. The presence of zeolites in concretes with basaltic aggregates is also referred to in some published papers from Argentina.

Besides the case studies of concrete structures affected by ASR due to volcanic aggregates, there are also several tests conducted in the laboratory that consider these rocks potentially reactive. Among the volcanic rocks studied by different researchers, the basalts from Argentina, Australia, Brazil, Czech Republic, Iceland, Japan, Turkey and USA (Hawaii) were considered potentially reactive either by the petrographic method or/and AMBT mainly because of the presence of volcanic glass, in some cases associated with clay minerals. However, according to several researchers the AMBT is not a reliable method and should not be used alone to assess the alkali-reactivity of an aggregate. There are a few cases reported where basalts were also considered reactive by the CPT (38°C, 1 year or similar method), such as the case of some basalts from Argentina, Australia and the USA (Hawaii). In Argentina, the reaction was due to the presence of silica minerals (e.g. cristobalite and tridymite) (Milanesi, 2008). In the Australian example, opaline silica was identified in the carbonate minerals present in the basalt (Shayan and Quick, 1988). In the case of Hawaii, petrographic analysis was unfortunately not performed to know which aggregates were causing the expansion (Robertson and Shen, 2018).

Basaltic rocks have low silica (SiO_2) content but can contain silica-rich volcanic glass that is considered potentially reactive. Besides volcanic glass, they can also contain other deleterious phases such as reactive forms of silica (e.g., opal, chalcedony, tridymite, cristobalite and micro- to cryptocrystalline silica). Clay minerals are also present in these rocks but their reactivity is not considered by the RILEM recommendations although some researchers classify them as deleterious phases. Some clay minerals have already an expansive characteristic due to their nature and structure, which can further contribute to the expansion; however, this is not related to alkali-silica reaction per se.

The methodology used in the present work confirmed that similar aggregates can contain distinct petrographic characteristics with different quantities of a volcanic glass of diverse composition and variable mineral composition. It was verified that all the aggregates considered potentially reactive by the AMBT method contain volcanic glass identified by petrography and confirmed by EMPA. However, not all the aggregates that contain volcanic glass induced significant expansion in the AMBT. On the other hand, the results of the petrographic examination of the mortars and concrete after completion of the expansion testing are in accordance with those obtained from the AMBT and CPT results. This means that whenever the results classify the aggregates as potentially reactive/reactive, the petrography confirms the presence of mainly cracks with gel crossing or outlining aggregate particles, for both tests. As for the AMBT and CPT methods, there is a correlation regarding the end results of both tests in 78% of the studied cases (i.e. reactive/reactive; non-reactive/non-reactive – see figure 6.1). On the other hand, 22% of the aggregates tested induced high expansion in the AMBT without generating significant expansion in the CPT. This suggests that the AMBT is somewhat more conservative although it may result in “false-positive” results (Figure 6.1).

The DRI method helped confirm that most of the concrete slabs showing severe to very severe signs of ASR correspond to the aggregates where volcanic sand was used as fine aggregates. The other cases are related to the andesites from Japan and Turkey samples and to Spratt siliceous limestone which is a well-known reactive aggregate, here used as a control sample. The results of the DRI can be correlated with GPT, whenever the gel is present in several sand particles. Also, the higher values of DRI can be directly correlated with the results obtained for the aggregates considered reactive in the CPT method.

Some general conclusions can be made from the aggregates from the Islands and Continental regions selected for this study.

Aggregates from the Islands:

- A large number of basaltic aggregates contain volcanic glass, except for most of the rock samples from the Azores, where glass is rare. All aggregates from Hawaii and Iceland contain volcanic glass;
- The chemical composition of volcanic glass in the volcanic aggregates ranges from 62 to 80% of SiO₂. The Hawaiian aggregates have the highest values (e.g., dacitic to rhyolitic volcanic glass), followed by NZ3 (from New Zealand) with a range between 53% to 71% of SiO₂;
- Clay minerals are present in several aggregates in the form of smectite and chlorite;

- The gravel samples from Iceland contain a mixture of rocks that includes mainly basalt, glassy basalt, rhyolite and less dacite. The presence of volcanic glass was identified in all the rocks and silica minerals in the last two;
- Most of the fine aggregate samples are reactive in all the methods except for ICL3 sand (Iceland) and HW4 sand (Hawaii);
- The high DRI obtained for the FLO-SM1 sample (Azores) is peculiar because all the other methods classified this rock sample as non-reactive. Possibly another type of deterioration is occurring and needs to be further investigated. Until new studies and data is gathered, it is recommended not to use this aggregate on critical concrete infrastructures;
- The JAP sample (Japan) is considered reactive by all methods due to the presence of tridymite. A DRI value of 1208 was obtained on the test specimen after the CPT, where the degree of concrete deterioration is considered severe to very severe,

Aggregates from Continental regions

- The sample of basalt from Brazil has the highest SiO₂ content (about 59% in the bulk chemical analysis) when compared to the other basalts from Continental regions. It contains also abundant clay minerals, in the form of clay minerals quartz and chalcedony;
- The older basalts, namely Canada and Norway samples, are considered not reactive in all the methods used;
- The Mozambique sample is considered potentially reactive by petrography due to the presence of volcanic glass (~67% SiO₂) and tridymite and according to the AMBT method. Also, the gel is present on many particles in the GPT. However, the CPT method classifies this aggregate as non-reactive and the DRI result is very low (DRI=37) considering this concrete is in good condition;
- The TK sample (Turkey) is considered reactive by all methods due to its intermediate character. The glassy groundmass contains an average SiO₂ content of 72%. A DRI value of 903, where the degree of concrete deterioration is considered severe to very severe, was obtained on the test specimen at the completion of the CPT. The reactivity of this aggregate is consistent with other works published in earlier years;
- Spratt limestone, the control aggregate, is considered reactive in all the methods used, as expected.

In addition, the following conclusions can be outlined from the present work:

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- The petrographic characterization of the aggregates was essential to identify volcanic glass as the main potentially alkali-silica reactive component in basalts and in the other volcanic aggregates investigated;
 - All the basaltic rocks that are reactive in the AMBT contain volcanic glass but not all the basaltic rocks with volcanic glass are considered reactive in the AMBT;
 - The Hawaiian aggregates are the only basaltic aggregates that contain silica-rich volcanic glass (dacitic to rhyolitic in composition). Also, these aggregates are considered oversaturated in silica;
 - The mortar bar test (AMBT) proved to be more sensitive to the volcanic aggregates than the CPT, causing several “false-positive” (22% of the aggregates tested). Thus, the AMBT is overestimating the reactivity for many basalts. This is probably due to the influence of the high temperature (80°C) of the test on the volcanic glass, especially with high content of SiO₂. These results show that this method is too conservative to evaluate the reactivity in basalts and should not be used as the only method to classify the potential alkali-reactivity of this type of rock; it should be mentioned that the AMBT and CPT tests classify similarly the aggregates as not reactive or reactive in 78% of the cases studied;
 - Most of the tested fine aggregates are considered reactive by all methods (Icelandic ICL1 coarse sand, ICL1 fine sand, ICL4 sand, GBS sand and Hawaiian HW7sand). The sand fraction is responsible for the reactivity in the CPT, since testing involved a non-reactive (reference) coarse high-purity limestone aggregate. This reactivity appears to be attributed to the particle size and the pessimum proportion; in the case of the pessimum proportion, the reactivity decreases with the increase in the content of the aggregate which is the case for rhyolitic and dacitic glass (100%);
 - Japan and Turkey samples are considered reactive by all methods. This is due to their intermediate character and the composition of the volcanic glass;
 - The control aggregates, Spratt limestone and GBS sand are also considered reactive by all methods;
 - Mozambique sample is considered non-reactive according to the CPT and the DRI results;
 - The high values of DRI obtained for the test prisms incorporating the volcanic sands are correlated with the presence of gel in several sand particles in the GPT;
 - The higher values of DRI correspond to the aggregates considered reactive in the CPT;
 - The results obtained by the different methods seem to point out that the basalt coarse aggregates studied are considered non-reactive. The volcanic glass present in the

above aggregates seems to be sensitive to the high temperature in the AMBT method, especially when glass is richer in silica. The reactivity when existent is associated with the volcanic sand fraction, even of basaltic composition (e.g. Hawaiian aggregate HW7 sand), that is observed in most of this type of mixtures. This seems connected to the particle size and pessimum proportion in the aggregate.

7.2. Future research

The assessment of the investigation done for all the volcanic aggregates studied in the present work allowed to point out some issues that must be further investigated, namely by other researchers with the skills to develop this specific domain of science or in the scope of other research projects. Some of this research should include the following issues:

- Assessment of field structures in which basalts have been used to verify the results of this research;
- Develop research to explain the different behaviour in mortar and concrete prism test;
- Eventually create a new test method for this type of rocks;
- Understand why some rhyolites are not reactive in the CPT;
- Further analysis of volcanic glass of selected aggregates (issues with EPMA readings on glass material);
- Complete full mineralogical characterization of the sands to better understand behaviours in AMBT and CPT; investigate further some “peculiar” behaviours:
 - HW7 aggregates (HW7 FA (fine aggregate); HW7 CA (coarse aggregate); HW7 FA + CA);
 - IC1 sands (fine and coarse sands – AMBT vs CPT results – effect of particle size);
- Conduct AMBT and CPT at different temperatures on selected aggregates (with various glass content) to investigate the effect of temperature on expansion → better understand glass activation as a function of temperature; compare behaviour vs SiO₂ content of the glass;
- Quantify the amount of glass in some aggregates and look at correlation with expansion in the AMBT, CPT (pessimum effects)

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