NEW INVESTIGATIONS ON THERMAL MANIFESTATIONS OF S. MIGUEL (AZORES)

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The scientific interest for the thermal manifestations of S. Miguel dates back to Fouqué, whose results were published in 1873, while further contributions were given by Lepierre (1912) and Herculano de Carvalho (1953).

In 1969 Quintino in his study on the hydrothermal system of Furnas stressed the importance of the chemical analyses of the fumaroles and the thermal waters as an investigation tool in determining the characteristics of subsoil fluid circulation.

Apart from the more important researches carried out by the S. Miguel geothermal project, this paper is aimed to give a short up-to-date contribution on the basis of some chemical data obtained by surface sampling of fumaroles and thermal springs from Furnas and Agua de Pau areas.

Figure 1 shows the locations of the studied manifestations, which include also some cold waters.

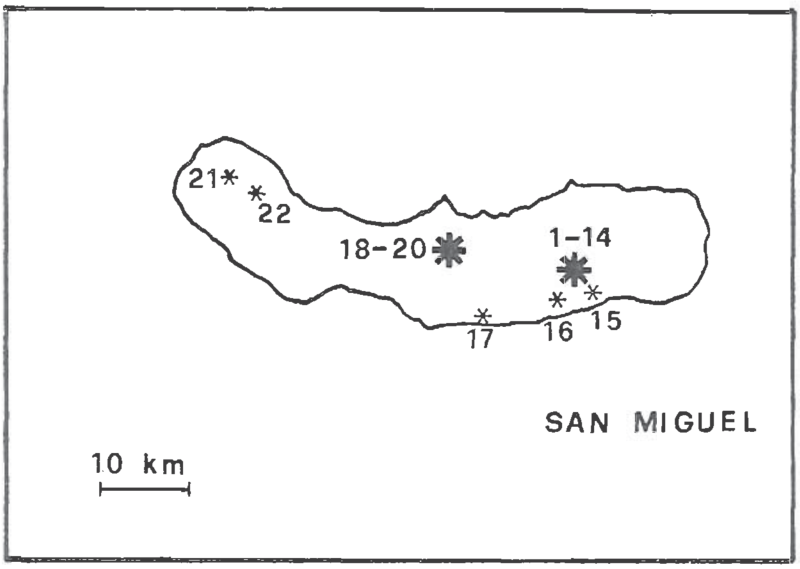

Figure 1 — Locations of the studied manifestations.

Table Ia and Ib give the analytical data for the waters.

The square diagram of fig. 2 allows to distinguish two different families, by the chemical standpoint, of bicarbonate and sulphate waters.

In considering the waters of bicarbonate composition it is easy to observe (fig. 3) that their pH values, ranging from 5.16 to 7.78, are correlated with the temperature. The weak acidity of these waters appears due to the greater solubility of carbon dioxide at lower temperatures.

Instead, the stronger acidity of sulphate waters is probably the result of surface oxidization of sulphur species, which allows a higher degree of rock alteration.

By a simple statistical cluster analysis it is possible to depict the fundamental associations between the investigated chemical characters (fig. 4). The resulting two main branches

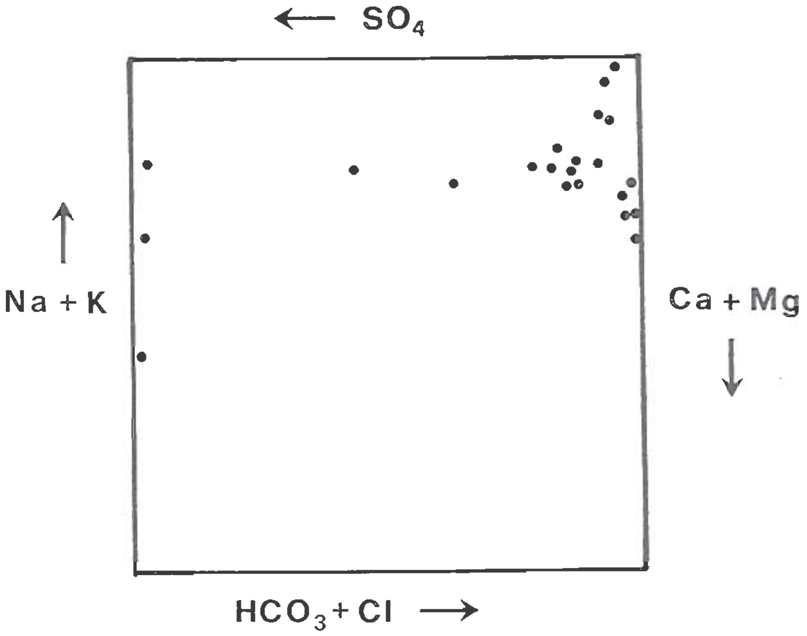

Figure 2 — Square diagram representing the fundamental chemical composition.

point out the preferential grouping of chemical quantities which can correspond to different chemical processes, possibly giving rise to the observed different hydrochemical types.

In other words, the variables of the right branch should correspond to leaching of rocks by weakly acid hydrogencarbonate waters, giving rise to the bicarbonate type, while the other parameters should pertain to a stronger alteration process in acid environment, with resulting sulphate solutions.

The temperature was not considered by this statistical procedure since the surface measurements could give values not completely reliable.

Geothermometers based on concentrations of specific chemical indicators give sometimes deceiving information ; in our

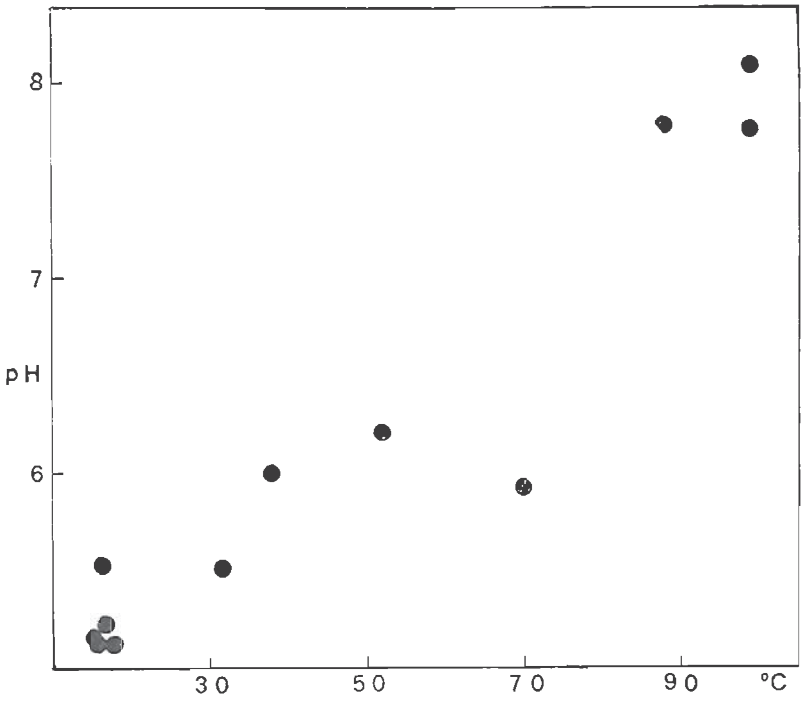

Figure 3 — Correlation between temperature and pH values of waters of bicarbonate type.

case, either the SiO_2 or the Na/K geothermometer, if applied to the samples 9 and 10 with the highest temperatures and possibly the least affected by superficial changes, give values around 100°C.

The observed temperature of the first confined aquifer encountered by a drilling in Agua de Pau area at a depth of about 150 m is around 110°C; since the inference of a similar hydrogeological pattern for the area of Furnas does not seem unreasonable, we can assume the calculated temperature as representative of a shallow confined aquifer.

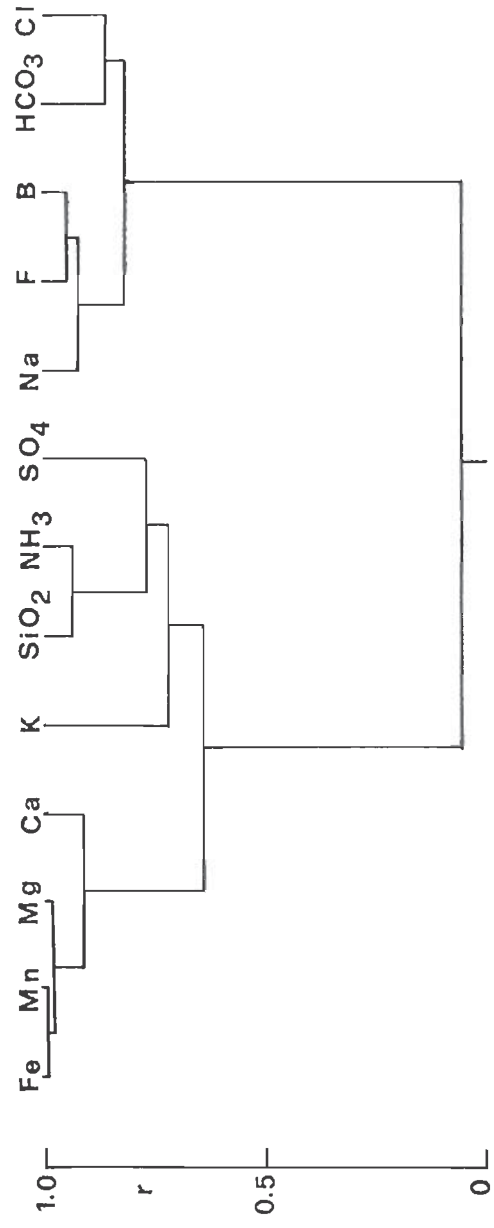

Figure 4 — Dendrogram resulting from a statistical cluster analysis of the chemical constituents.

The same calculating procedure cannot be safely applied for the other samples because:

a) the acid waters of sulphate type presumably reflect a non-equilibrium situation of present alteration of rocks, yet not fulfilling a main condition of geothermometry;

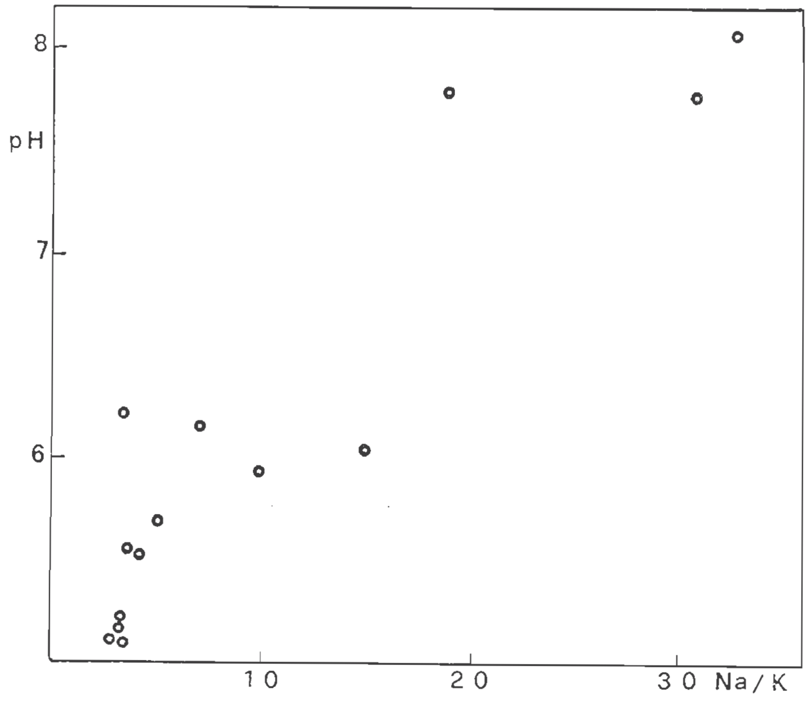

Figure 5 — Correlation between Na/K ratios and pH values of waters of bicarbonate type.

b) the remaining waters of bicarbonate type show Na/K ratios depending on pH values (fig. 5); this can be ascribed to different degrees of leaching of rocks, with enrichment of K with respect to Na, due to the above

> mentioned greater solubility of carbon dioxide in deep waters cooled by mixing with surface solutions ; the again resulting non-equilibrium situation prevents any correct geothermometry.

The sodium bicarbonate waters appear to represent the shallow boiling aquifer outflowing in the low areas of Caldeiras das Furnas and Ribeira Quente. Samples 9 and 10 seem to keep better the original chemical-physical characters, while all the other samples pertaining to this group are the result of different degrees of dilution by surface waters.

At higher elevation this boiling aquifer is confined, but possible fractures can allow the escaping gases to reach the surface ; their condensation gives rise to acid solutions, with increased degree of alteration of rocks and the observed change in chemical character. The surface acid waters are to be considered as an evidence of the deeper confined boiling aquifer.

Keeping into account the trace elements distribution, the ratio NH_4/Li seems well apt to discriminate between the two outlined genetic processes ; while both lithium and ammonia can be present in the boiling aquifer, ammonia only is allowed to migrate upwards in the gaseous form. The observed values of the NH_4/Li ratio in the investigated samples fit rather well this hypothesis.

With reference to the main composition of the bubbling gases, the data from Caldeira de Esguicho and Ribeira Grande manifestations (table II) respectively of bicarbonate and sulphate type, point out a higher ratio of gas to water in the second kind of waters, again strenghtening the previous assumptions.

A systematic survey of chemical composition of ground waters, with special reference to the elements whose mobility can be to a large extent influenced by changes in the chemical-physical conditions of the subsoil environment, besides its importance for geothermal purposes, can act as a simple but effective tool in surveillance of active or potentially active volcanic areas.

Obviously, the chemical changes of ground waters cannot reflect short-time variations of the actual thermodynamic conditions, but can provide an integrated picture of some major trends in compositional characters well in advance of the establishing of critical conditions, thus allowing a long-term forecast.

Although the experiences on this subject are few and very recent, the usefulness of such a simple tool should not be underevaluated.

REFERENCES

CASTELO BRANCO, A., ZBYSZEWSKY, G., MEDEIROS, A. C. and ALMEIDA, F. M. (1957) : Etude géologique de la region de Furnas dans l'île de S. Miguel (Açores). Lisboa.

FOUQUE, F. (1873) : Les eaux thermales de l'île de S. Miguel (Açores). Lisboa.

HERCULANO DE CARVALHO, A. (1955) : Estudos analíticos de águas termais. (Direcção Geral de Minas e Serviços Geológicos, Lisboa).

LEPIERRE, C. (1917) : Análise das águas minero-medicinais do vale das Furnas. Ilha de S. Miguel, Lisboa.

MARTINI, M. and CELLINI LEGITTIMO, P. (1977) : Sul contenuto di ammonio in acque termali. Rend. Soc. It. Min. Petr., 33, p. 781-790.

MUECKE, G. K., ADE-HALL, J. M., AUMENTO, F. MACDONALD A., REYNOLDS, P. H., HYNDMAN, R. D., QUINTINO, J., OPDYKE. N. and MOWRIE, W. (1974) : Deep drilling in an active geothermal area in the Azores. Nature, 252, p. 281-284.

QUINTINO, J. (1969) : Sistemas hidrotermais associados ao vulcanismo e sua prospecção com fins económicos. Aplicação à região das Furnas (S. Miguel — Açores). Técnica, Lisboa.

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TABLE Ia

Number	Sample location	Temp.	pH	Cond.	Ca	Mg	Na	K	HCO_3	SO_4	Cl
1	Lagoa das Furnas	78	2.81	1.8	4.6	4.5	5.6	.98	—	23	.15
2	Lagoa das Furnas	15	5,59	.16	.25	.22	1.2	.24	1.3	.06	.41
3	Lagoa das Furnas	20	7.02	.13	.17	.18	.86	.19	.69	.61	.35
4	Prata	32	5.51	.32	.60	.30	2.2	.53	2.8	.47	.40
5	Miguel Henrique	16	5.52	.28	.43	.20	2.1	.56	2.2	.51	.49
6	Água Santa	88	7.78	.81	.22	.05	9.8	.52	6.7	.35	1.4
7	Caldeirão	70	5.93	.44	.46	.29	4.2	.41	4.0	.51	1.1
8	Rebentão	15	5.16	.23	.55	.33	1.5	.48	1.8	.35	.48
9	Caldeira de Esguicho	99	7.77	1.4	.17	.02	17	.55	9.6	1.3	6.3
10	Caldeira Grande	99	8.06	1.8	.19	.02	22	.64	12	1.6	8.2
11	Doutor Dinis	16	5.11	.26	.37	.28	1.6	.49	1.8	.36	.45
12	Chalet Frio	16	5.20	.28	.42	.28	1.7	.55	1.8	.60	.50
13	Água Azeda	15	5.13	.27	.37	.31	1.6	.53	1.9	.38	.43
14	Caldeira dos Vimes	56	6.23	.35	.45	.33	2.1	.63	1.2	2.1	.42
15	Ribeira Quente	38	6.03	1.2	2.8	1.2	11	.73	7.8	1.4	6.2
16	road to Furnas	14	7.73	.20	.30	.23	1.7	.15	1.0	.46	1.1
17	Água de Pau	16	7.68	.12	.19	.15	.91	.13	.64	.05	.58
18	Ribeira Grande	87	2.38	3.0	.95	.63	2.2	.70	—	16	.60
19	Ribeira Grande	17	6.16	.11	.10	.15	.83	.12	.86	.01	.52
20	Caldeira Velha	87	2.90	1.2	.32	.40	1.9	.78	—	8.0	.24
21	Lagoa das Sete Cidades	24	7.40	.09	.17	.11	.64	.06	.39	.05	.42
22	Canário	15	7.11	.14	.22	.28	.91	.16	1.0	0.2	.44

Table Ia — Fundamental chemical composition of the studied waters. Values are expressed as milliequivalents per liter ; specific conductivity is given in millimhos.

TABLE Ib

Number	*SiO₂*	*B*	*F*	*Li*	*NH₄*	*Sr*	*Fe*	*Mn*
1	7.0	.001	.23	.001	.55	.018	3.6	.23
2	1.2	.001	.047	.001	.012	.018	—	—
3	.50	.001	.046	.001	.030	.018	.007	.003
4	2.1	.001	.11	.003	.016	.023	.22	.021
5	1.7	.001	.12	.002	.005	.023	.066	.017
6	2.3	.49	.34	.018	.052	.001	—	.002
7	3.0	.16	.12	.007	.021	.025	.033	.021
8	1.9	.015	.13	.001	.012	.001	.20	.014
9	2.1	1.1	.70	.035	.018	.028	—	.001
10	2.2	1.4	.92	.045	.043	.001	—	—
11	1.9	.001	.052	.001	.042	.001	.065	.012
12	1.8	.020	.050	.001	.069	.001	.017	.018
13	1.8	.001	.050	.001	.050	.001	.076	.018
14	1.5	.001	.067	.001	.066	.001	.010	.014
15	2.8	.066	.25	0.18	.009	.037	.25	.034
16	1.1	.020	.059	.001	.007	.001	—	—
17	1.0	.030	.038	.001	.005	.001	—	.019
18	4.6	.046	.24	.002	.13	.028	.57	.022
19	1.2	.002	.050	.001	.004	.005	—	—
20	8.0	.066	.20	.003	.62	.021	.53	.033
21	.001	.001	.024	.001	.037	.003	—	—
22	.90	.001	.016	.001	.035	.001	—	—

Table Ib — Concentrations of minor constituents in the studied samples. Values are expressed as milliequivalents per liter for F, Li, NH_4, Sr, Fe, Mn, and as millimoles per liter for SiO_2 and B.

TABLE II

	H_2O	CO_2	H_2S	gas/water lt/kg
Caldeira de Esguicho	92.8	7.1	0.03	96
Ribeira Grande	81.1	18.7	0.02	289

Table II — Volume percentage composition of the bubbling gases.