Gaseous emanations from Azores volcanic lakes: geochemical characterization

Tese de Doutoramento

César Cristóvão Costa Andrade

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César Cristóvão Costa Andrade

Orientadores

Professor Doutor José Virgílio de Matos Figueira Cruz

Professora Doutora Maria de Fátima Batista Viveiros

Tese especialmente elaborada para obtenção do grau de Doutor em Geologia

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Preliminary Note

I hereby testify that this thesis was of my own initiative, specially developed to this purpose. This thesis includes a version of five original papers submitted and published in indexed scientific journals (one of which currently under revision), the inclusion of co-authors reflects the fact that the work resulted from active collaboration between researchers and acknowledges input into team-based research, as shown the following papers below:

Andrade, C., Viveiros, F., Cruz, J.V., Coutinho, R., Silva, C., 2016. Estimation of the CO_2 flux from Furnas Volcanic Lake (São Miguel, Azores). *J. Volcanol. Geotherm. Res.* 315, 51-64. http://dx.doi.org/10.1016/j.jvolgeores.2016.02.005.

C. Andrade, F. Viveiros and J.V. Cruz designed the investigation. C. Andrade conducted the data collection, both in the field and the laboratory, and was responsible for the data analysis. F. Viveiros and J.V. Cruz collaborated on the original draft preparation and methodology adjustments. All co-authors also contributed to manuscript editing and reviewing.

Andrade, C., Viveiros, F., Cruz, J.V., Branco, R., Moreno, L., Silva, C., Coutinho, R., Pacheco, J., 2019. Diffuse CO_2 flux emission in two *maar* crater lakes from São Miguel Island (Azores, Portugal). *J. Volcanol. Geotherm. Res.* 369, 188-202. http,//dx.doi.org/ 10.1016/j.jvolgeores.2018.11.030.

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Andrade, C., Viveiros, F., Cruz, J.V., Coutinho, R., Branco, R., 2019. CO_2 fluxes of two lakes in volcanic caves in Azores, Portugal. *Appl. Geochem*. 102: 218-228 http://dx.doi.org/ 10.1016/j.apgeochem.2019.02.006.

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C. Andrade, F. Viveiros and J.V. Cruz designed the investigation. C. Andrade conducted the data collection, both in the field and the laboratory, and was responsible for the data analysis. F. Viveiros and J.V. Cruz collaborated on the original draft preparation and methodology adjustments. All co-authors also contributed to manuscript editing and reviewing.

Andrade, C., Cruz, J.V., Viveiros, F., Branco, R., Coutinho, R., 2019. CO_2 degassing from Pico Island (Azores, Portugal) volcanic lakes. *Limnologica* (under review).

C. Andrade, F. Viveiros and J.V. Cruz designed the investigation. C. Andrade conducted the data collection, both in the field and the laboratory, and was responsible for the data analysis. F. Viveiros and J.V. Cruz collaborated on the original draft preparation and methodology adjustments. All co-authors also contributed to manuscript editing and reviewing.

César Cristóvão Costa Andrade

Ponta Delgada, março 2019

“Fairy tales are more than true: not because they tell us that dragons exist, but because they tell us dragons can be beaten”

(*Neil Gaiman*)

À Sónia

Dedico com carinho

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Abstract

In the Azores Archipelago, formed by nine Islands of volcanic origin, exist several lacustrine systems whose genesis and hydrologic and hydrogeochemical characteristics are related to the geological origin of the archipelago.

Located on the North Atlantic at the vicinity of the triple junction of the North American, Eurasian and Nubian plates, which originates intense seismic and volcanic activity, the Azores Archipelago, due to its geodynamic and geostructural framework, constitutes a natural laboratory for the study of phenomena linked to secondary volcanism. As a matter of fact, manifestations of secondary volcanism such as fumarolic fields, thermal and/or CO_2 rich waters, as well as soil and lake surface diffuse degassing, which are the target of this study, can be observed on several islands of the Archipelago.

With the aim of characterizing and quantifying diffuse degassing on the volcanic lakes which exist in the archipelago, a study was performed on 45 water bodies dispersed across six islands. Fieldwork comprised water sampling at several depths along vertical profiles, as well as measurements of CO_2 degassing at lake surface. Whenever possible, two sampling surveys, one during winter and another in summer, were carried out.

Hydrogeochemical characterization lead to the conclusion that some lakes exhibit monomitic behavior, with water column stratification during the warmer period of the year, implying the occurrence higher carbon dioxide concentrations in the hypolimnion and the neutralization of water acidity promoted by water-rock interaction, which also leads to a bicarbonate enrichment. This process is not observed during winter, which allows for good water mixing along the water column with no CO_2 retention at the bottom. In these conditions, dissolved CO_2 concentrations at the bottom are significantly reduced.

Eutrophication, a process that affects several lakes in the Azores, also contributes to the increase of CO_2 emissions of biogenic origin. In some lakes, the existence of water surfaces covered by dense masses of macrophyte algae is also responsible for the increased concentration of some physical and chemical parameters, mainly CO_2.

Apart from the contribution of free CO_2 resulting from the degradation of organic matter accumulated at the bottom of the lakes, a component clearly linked to the water contamination by fluids of magmatic origin was also identified, namely at Furnas and Santiago lakes (on São Miguel) and Furna do Enxofre Lake (Graciosa).

Prevailing hydrogeochemical facies are sodium chloride, which derives from atmospheric marine salts contamination, and, albeit not to the same extent, sodium

bicarbonate as the result of water-rock interaction, as well as the intermediate type of these two facies. Water from Furna do Enxofre exhibits a dissimilar bicarbonate magnesium type.

Concerning CO_2 flux, 16119 measurements were performed, with values ranging from 0 to 20960 g m^{-2} d^{-1} (average = 54 g m^{-2} d^{-1}). The application of the GSA method for statistical analysis permitted the identification of different populations, which in some cases are associated to hydrologic processes that occur in the lakes, while in others, these are linked to volcanic fluids contamination.

In the lakes where stratification occurs and where it was possible to run two sampling surveys, namely one during summer (when stratification is observed) and another during winter (with no stratification), significant differences on the estimated CO_2 output were recorded. This is explained by the CO_2 being retained in the hypolimnion when lakes suffer stratification during the warmer summer period. This behaviour is not observed in shallower lakes, where CO_2 flux values do not show significant variation year-round.

A relation was established between CO_2 anomalous areas and tectonic structures that cross some of the studied lakes. It was possible to conclude that some of these anomalous areas coincide with existing tectonic features, suggesting that these structures are preferential paths for deep gas fluxes of volcanic and/or hydrothermal origin.

The study of stable isotopic contents permitted not only the confirmation of the meteoric origin of studied waters, but also, based on $\delta^{13}C$ content, permitted to conclude that a fraction of the emitted CO_2 at Furnas, Santiago and Lagoa do Enxofre lakes is of deep origin. In the remaining lakes, $\delta^{13}C$ water content proves that emitted CO_2 has a biogenic origin, even when more than one set of CO_2 flux data was identified.

Estimated values of emitted CO_2 permit to conclude that the studied lakes emit CO_2 amounts to the atmosphere between 0.0003 t d^{-1} (Algar do Carvão_1) and 600 t d^{-1} (Furnas_2). Relating the output values and the lakes' surface areas, values range between 0.003 t km^{-2} d^{-1} (Achadas) and ~530 t km^{-2} d^{-1} of CO_2 (Furna do Enxofre). The amounts emitted by Furna do Enxofre make it possible to position this water body amongst the five lakes of volcanic origin worldwide with the highest emission of CO_2 into the atmosphere. Considering the calculations of CO_2 emissions from all studied lakes, the total CO_2 flux released in the Azores has an estimated value of ~383 t d^{-1}.

The results of the present work may be used as a reference value for seismovolcanic monitoring in the Azores, considering that significant changes in these emission rates

may constitute sound evidence of alterations originating in depth, mainly in the volcanic systems where these water bodies are located.

Resumo

No arquipélago dos Açores, constituído por nove ilhas de origem vulcânica, ocorrem numerosos sistemas lacustres, cuja génese e características hidrológicas e hidrogeoquímicas se relacionam com a origem geológica do arquipélago.

Fruto do seu enquadramento geodinâmico e geoestrutural, o arquipélago dos Açores, localizado no Atlântico Norte e, em particular, nas proximidades da junção tripla entre as placas litosféricas Norte Americana, Euroasiática e Núbia, de que resulta uma intensa atividade sísmica e vulcânica, apresenta-se como um laboratório natural para o estudo de fenómenos associados ao vulcanismo secundário. Com efeito, em várias ilhas do arquipélago ocorrem manifestações de vulcanismo secundário, nomeadamente campos fumarólicos, nascentes de águas termais e/ou gasocarbónicas, assim como zonas de desgaseificação difusa através dos solos e da superfície dos lagos, matéria esta estudada na presente dissertação.

Com o objetivo de proceder a uma caracterização e quantificação da desgaseificação difusa através dos lagos vulcânicos existentes no arquipélago dos Açores, foi realizado um estudo em 45 destas massas de água, dispersas por seis ilhas. No decurso dos trabalhos de campo foram efetuadas amostragens de água através de perfis verticais, a várias profundidades, assim como medições do fluxo de dióxido de carbono libertado à superfície destes lagos. Sempre que possível, e por forma a compreender o efeito da sazonalidade sobre os resultados obtidos, realizaram-se pelo menos duas campanhas de amostragem, uma no período de inverno e outra no período de verão.

A caracterização hidrogeoquímica permitiu constatar que alguns lagos apresentam um comportamento monomítico, com estratificação da coluna de água no período mais quente do ano, implicando a ocorrência de concentrações de dióxido de carbono mais elevadas no hipolimnion e sendo a neutralização da acidez da água promovida pela interação água-rocha, o que acarreta um enriquecimento também em bicarbonato. Já durante o inverno este processo não é observável, o que permite, assim, que ocorra uma mistura da água ao longo de toda a coluna de água, não ficando, desta forma, o CO_2 retido em profundidade. Nestas condições, registam-se concentrações de CO_2 dissolvido na água significativamente mais reduzidas em profundidade.

A eutrofização, processo que afeta muitos lagos no arquipélago dos Açores, também contribui para o incremento das emissões de CO_2 de origem biogénica. Em particular, a presença de áreas cobertas por massas densas de algas e macrófitas em alguns

lagos também é responsável pelo incremento nas concentrações de alguns parâmetros físico-químicos, em especial de dióxido de carbono.

Para além da contribuição do CO_2 livre a partir da degradação da matéria orgânica acumulada nos lagos, foi ainda identificada, em alguns casos, uma componente claramente associada à contaminação da água por fluidos de origem magmática, nomeadamente na lagoa das Furnas e de Santiago (São Miguel) e na Lagoa da Furna do Enxofre (Graciosa).

As fácies hidrogeoquímicas predominantes são a cloretada sódica, que deriva principalmente da contaminação por sais de origem marinha a partir do transporte atmosférico, e a bicarbonatada sódica, embora esta última seja menos significativa, que indica uma contribuição por interação água-rocha, assim como os tipos intermédios a estes. A água da Furna do Enxofre apresenta um tipo distinto dos anteriores, nomeadamente bicarbonatada magnesiana.

No que concerne à medição do fluxo de CO_2, foram realizadas 16119 medições, tendo-se registado valores entre 0 e 20960 g m^{-2} d^{-1} (média = 54 g m^{-2} d^{-1}). A análise estatística através do método GSA permitiu identificar a presença de diferentes populações, que em alguns casos estão associadas com os processos hidrológicos que ocorrem nos lagos, enquanto noutros estão associadas à contaminação de fluidos vulcânicos.

Nos lagos que estratificam e onde foi possível efetuar duas campanhas de amostragens, nomeadamente uma no verão (com estratificação) e outra durante o inverno (sem estratificação), foram registadas diferenças significativas no *output* estimado para a emissão de CO_2. Este facto explica-se pela retenção do CO_2 no hipolimnion quando os lagos se encontram estratificados durante o período mais quente do ano (verão). O mesmo não ocorre em lagos pouco profundos, que não só estratificam como não denotam variações nos valores de fluxo de CO_2 emitidos nos períodos de verão e de inverno.

Foram ainda relacionadas as zonas anómalas de CO_2 com as estruturas tectónicas que atravessam, em alguns casos, os lagos em estudo. Foi possível concluir que algumas destas zonas anómalas coincidem com os acidentes tectónicos presentes nestas áreas, sugerindo que estas últimas são estruturas preferenciais de libertação de gases de origem profunda, com origem vulcânica/hidrotermal.

O recurso ao conteúdo em isótopos estáveis permitiu não só confirmar a origem meteórica das águas estudadas, como ainda, a partir dos valores de $\delta^{13}C$, concluir que uma fração do CO_2 emitido nas lagoas das Furnas, da Furna do Enxofre e de Santiago é

de origem profunda. Nos restantes lagos, a composição da água em $\delta^{13}C$ demonstra que o CO_2 emitido é de origem biogénica, mesmo no caso em que foram identificadas mais do que uma população de dados de fluxo de CO_2.

Os valores estimados de emissão de CO_2 permitem concluir que os lagos estudados emitem para a atmosfera valores entre os 0,0003 t d^{-1} (Algar do Carvão_1) e 600 t d^{-1} (Furnas_2) de CO_2. Relacionando os valores de output com as áreas superficiais dos lagos, os valores situam-se entre 0,003 t km^{-2} d^{-1} (Achadas) e ~530 t km^{-2} d^{-1} de CO_2 (Furna do Enxofre). Neste último caso, os valores estimados permitem sugerir que esta massa de água se posiciona entre os cinco lagos de origem vulcânica que emitem mais CO_2 para a atmosfera a nível mundial. Somando a emissão de CO_2 estimada de todos os lagos estudados neste trabalho, o fluxo total de CO_2 libertado nos Açores corresponde a um valor estimado de ~383 t d^{-1}.

Os resultados da presente investigação poderão servir de base à monitorização sismo-vulcânica nos Açores, uma vez que quaisquer alterações significativas nestes valores agora conhecidos podem constituir evidências de alterações em profundidade, principalmente nos sistemas vulcânicos onde se localizam estas massas de água.