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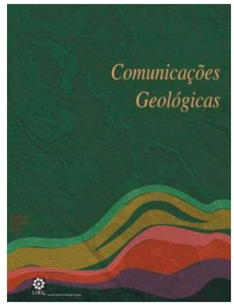
Comunicações Geológicas

Comunicações Geológicas (2020) 107, Especial I, 21-23
ISSN: 0873-948X; **e-ISSN:** 1647-581X

Fumarolic gas monitoring after an hydrothermal explosion at Caldeira do Asmodeu (Furnas Volcano, Azores)



Monitorização de emissões fumarólicas após explosão hidrotermal na Caldeira do Asmodeu (Vulcão das Furnas)

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Recebido em 28/02/2018 / Aceite em 16/12/2019
Publicado em agosto de 2020

Artigo original
Original article

Abstract: On the 30th of August 2017 an explosion occurred in Caldeira do Asmodeu fumarole located in the Furnas Village fumarolic field, São Miguel Island. Local inhabitants reported that the turbidity of the water increased before the explosion and all the water disappeared immediately after the event. Subsequently, the water appeared with a muddy aspect. Sampling of the gases released from a close fumarole was done the following day and one week after the explosion. Chemical analyses included gas chromatography for the gases in the headspace of the bottles and titration for those in the alkaline solution. Results obtained were compared with data gathered since 2015 and some ratios were applied to the gas compositions of the fumaroles before and after the explosion. The results obtained did not show significant differences and contributed to confirm that the phenomena should be quite superficial, thus not related with deep changes on the system.

Keywords: Hydrothermal explosion, Caldeira do Asmodeu, Furnas Volcano, gas ratios, hydrothermal fumaroles.

Resumo: No dia 30 de agosto de 2017 ocorreu uma explosão hidrotermal na fumarola designada por Caldeira do Asmodeu, localizada no campo fumarólico da freguesia das Furnas, Ilha de São Miguel. Os residentes relataram um aumento da turbidez da água nos dias precedentes à explosão e o desaparecimento de toda a água da fumarola após o evento. Posteriormente a água reapareceu com um aspeto lamacento. A amostragem dos gases libertados de uma fumarola próxima da Caldeira do Asmodeu foi efetuada no dia seguinte e repetida uma semana depois. As análises químicas incluíram cromatografia de fase gasosa para os gases retidos no espaço livre das ampolas de Giggenbach, e titulação para os da solução alcalina. Os resultados foram comparados com os dados obtidos desde 2015 para o que se aplicaram algumas razões por forma a detetar eventuais diferenças na composição dos gases antes e após a explosão. Os resultados obtidos contribuíram para confirmar que não existiram alterações significativas na composição química dos gases e que a explosão deverá resultar de fenómenos superficiais, e não de alterações no sistema em profundidade.

Palavras chave: Explosão hidrotermal, Caldeira do Asmodeu, Vulcão das Furnas, razões químicas, fumarolas hidrotermais.

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1. Introduction

Furnas Volcano, located on the eastern part of São Miguel Island, is formed by two nested calderas controlled by NW-SE and NE-SW faults (Guest *et al.* 1999). Nowadays, volcanic activity is characterized by fumaroles, steaming grounds, thermal and cold CO_2-rich springs as well as diffuse degassing areas (Ferreira *et al.* 2005; Viveiros *et al.* 2010). Most of the manifestations are located inside the caldera where there are three fumarolic fields and another one on the south flank of the volcano. Caldeira do Asmodeu (CA) is located in the Furnas village fumarolic field. This fumarole is marked for being a vigorously boiling fumarole with an emitted flux of CO_2 of approximately 17.8 t d^{-1} (Pedone *et al.,* 2015). In the last decade at least one person died at this site due to a fall in the fumarole. For safety reasons, direct gas sampling following the Giggenbach methodology is not suitable for this fumarole and it has been therefore done in Caldeira Seca, about 40 m far from CA. Hydrothermal explosions in Caldeira do Asmodeu have been reported in the 20th century (Ferreira, 1994), and the last one occurred on the 30th of August 2017. The aim of this work is to investigate if chemical changes have occurred after the explosion that can show signals of deep changes in the feeding reservoir system.

2. Sampling and analytical methodology

Gas samples were collected in Caldeira Seca fumarole using pre-vacuum Giggenbach bottles filled with NaOH 4N. The bottles were connected to an inverted funnel placed over the fumarole to catch and transfer the gas into the bottle (Giggenbach and Goguel, 1989). Analysis of the gas samples were done in the laboratory of gas geochemistry of the Research Institute for Volcanology and Risk Assessment (IVAR) of the University of the Azores, following the methodologies described by Caliro *et al*. (2015) and Moreno *et al*. (2016).

3. Results

Chemical analyses between 2015 and 2018 of Caldeira Seca fumarole show that the dominant gas in the dry phase is CO_2 with more than 98 molar%. Hydrogen sulphide (H_2S), hydrogen (H_2) and nitrogen (N_2) are the other components appearing in higher concentrations (> 0.1 molar%). Methane (CH_4), helium (He), oxygen (O_2) and argon (Ar) are present in minor concentrations (< 0.005 molar%). All the results are shown in table 1.

4. Discussion and conclusions

Study of different gas ratios can be very useful in any seismovolcanic monitoring programme since changes on these ratios may be associated with differences on the equilibrium conditions of the reservoirs that feed the gas emissions (Arnórsson, 2000). Some significant gas ratios are shown in table 2. The gas ratio CO_2/CH_4 has been described in literature (Chiodini *et al.*, 2009) as a good indicator of eventual unrest periods. H_2S/CO_2 ratio gives information about the deep boiling degree of the hydrothermal system associated to the fumarolic fields (Ellis and Mahon, 1977). CH_4/H_2 gives us more information about the state of equilibrium as the CH_4 is attributed to equilibrium reactions in deep aquifers that originate the fumaroles, while a H_2 increase is directly associated with the base temperature of the aquifer (Ellis and Mahon, 1977). Table 2 shows values for the different gas ratios between 2015 and 2018, and an average of 0.008 for H_2S/CO_2, 23897 for CO_2/CH_4 and 0.02 for CH_4/H_2 are observed. No significant change is observed in the gas ratios when the data obtained in the period after the hydrothermal explosion is compared with the other sampling periods. Even when compared with data from 2013 (Caliro *et al*., 2015), no significant changes are observed in general. The absence of geochemical changes in the gas emitted from the Caldeira Seca fumarole suggests that the explosions resulted from superficial phenomena and not from deep changes in the feeding reservoir. The maintenance of a regular sampling programme in this fumarolic field is important to monitor the system in order to recognize future signals of volcanic unrest.

Table 1. Chemical composition of Caldeira Seca fumarole on several surveys. a) technical limitations did not allow separate detection of Ar and O_2.

Tabela 1. Composição química da fumarola Caldeira Seca ao longo de várias campanhas. a) limitações técnicas não permitiram a deteção separada de Ar e O_2.

Fumarole	*Sampling date*	*Temperature* (ºC)	CO_2 (molar %)	H_2S (molar %)	CH_4 (molar %)	H_2 (molar %)	He (molar %)	N_2 (molar %)	O_2 + Ar (molar %)	O_2 (molar %)	Ar (molar %)	Gas Chromatograph
Caldeira Seca	23/07/2015	97.4	98.9	0.74	0.004	0.22	0.002	0.14		0.001	0.003	**Perkin Elmer Clarus 580**
	23/07/2015	97.4	98.9	0.76	0.004	0.23	0.003	0.13		0.0003	0.003	
	31/08/2017	98.7	98.8	0.78	0.004	0.22	0.002	0.16		0.005	0.003	
	31/08/2017	98.7	98.8	0.74	0.004	0.23	0.003	0.20		0.011	0.004	
	08/09/2017	98.8	98.9	0.75	0.004	0.23	0.002	0.15		0.0002	0.003	
	08/09/2017	98.8	98.8	0.79	0.004	0.23	0.002	0.15	0.004	a)	a)	
	20/09/2017	99.6	98.8	0.78	0.005	0.27	0.003	0.17		0.0004	0.004	
	20/09/2017	99.6	98.9	0.78	0.004	0.22	0.003	0.13		0.0004	0.003	
	24/01/2018	98.3	98.8	0.73	0.005	0.27	0.003	0.19	0.005	a)	a)	
	24/01/2018	98.3	98.8	0.68	0.004	0.23	0.002	0.22	0.005	a)	a)	

Table 2. Gas ratios for the chemical composition of Caldeira Seca fumarole. *Data from Caliro *et al.,* 2015.

Tabela 2. Razões de gases da composição química da fumarola Caldeira Seca. *Dados de Caliro *et al.,* 2015.

Sampling date	H_2S/CO_2	CO_2/CH_4	CH_4/H_2
21/09/2013 *	0.006	21850	0.02
23/07/2015	0.008	25444	0.02
23/07/2015	0.008	24645	0.02
31/08/2017	0.008	26157	0.02
31/08/2017	0.008	25499	0.02
08/09/2017	0.008	24960	0.02
08/09/2017	0.008	23686	0.02
20/09/2017	0.008	18848	0.02
20/09/2017	0.008	24324	0.02
24/01/2018	0.007	20442	0.02
24/01/2018	0.007	24965	0.02

Acknowledgements

This study was partially funded by the project EUROVOLC (EU-H2020, INFRAIA-02-201).

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