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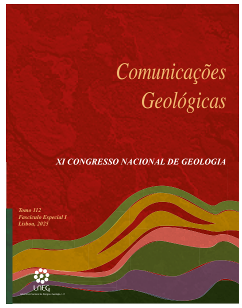
Investigating the hydrothermal activity at Fogo volcano (Cape Verde) using geochemical analyses of soil samples

Estudo da atividade hidrotermal no vulcão do Fogo (Cabo Verde) através da análise geoquímica de amostras de solo



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Abstract: Characterizing hydrothermal systems at volcanoes is particularly important as they play a crucial role in controlling eruptive dynamics. On the long term, hydrothermal systems participate in the geochemical alteration of both rocks and soils, through hydrolysis, dissolution, mineral precipitation, and secondary mineralization contributing in the gradual destabilization of volcanic structures. Fogo volcano (Cape Verde) is the most active volcano in the eastern Atlantic. It features a fumarolic field and passive degassing in its summit crater. A total of 65 soil samples were collected and analyzed, 4 years after the 2014-2015 eruption, in the area surrounding the volcanic edifice including the last eruptive vent with the main objective of detecting and identifying the geochemical and mineralogical signature of hydrothermal activity. Preliminary results show that soil samples were enriched in Ca, Cu, Co, Fe, Na, P, and Ti, when compared to 2014-2015 lava flows, which is confirmed by principal component analysis. Distribution of geochemical elements clearly reflects the mineral phases and is discussed together with geophysical data to shed the light on hydrothermal processes taking place at Pico do Fogo.

Keywords: volcanic soils, geochemistry, hydrothermal activity, Fogo volcano.

Resumo: A caraterização de sistemas hidrotermais em vulcões é relevante uma vez que estes desempenham um papel crucial no controlo da dinâmica eruptiva. A longo prazo, os sistemas hidrotermais têm influência na alteração geoquímica das rochas e dos solos, por hidrolise, dissolução, precipitação e mineralização secundária. O vulcão do Fogo (Cabo verde) é o mais ativo no Atlântico oriental. Um total de 65 amostras de solos foi recolhido, 4 anos após a erupção de 2014-2015, na área envolvente ao centro eruptivo, tendo sido realizada a caracterização geoquímica e mineralógica das amostras. Os resultados das amostras de solos revelaram enriquecimento em Ca, Cu, Co, Fe, Na, P e Ti, quando comparado com as lavas de 2014-2015, confirmado pela análise em componentes principais. A distribuição geoquímica reflete as fases minerais identificadas, o que será discutido com dados geofísicos para melhorar nossa compreensão dos processos hidrotermais no vulcão Pico do Fogo.

Palavras-chave: solos, geoquímica, atividade hidrotermal, vulcão do Fogo.

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1. Introduction

Hydrothermal circulation is a key component of volcanic systems that host a sustained magma reservoir. It constitutes an efficient way to transfer heat to the surface through porous rock/sediments and the hydrosphere (Renaut and Jones, 2011). When rising towards the surface, the hot and volatile-rich fluids interact with both host-rock and groundwaters. Hydrothermal alteration is then promoted by chemical reactions leading to acidification and consequently, mineral dissolution and precipitation with the formation of secondary minerals such clays (*e.g.*, illite) and/or silica polymorphs (*e.g.*, opal). Considering that hydrothermal circulation may either lead to the weakening or the strengthening of the host-rock (Heap *et al*., 2015), hydrothermal systems at volcanoes often assume a critical role in modulating eruptive dynamics. This study presents new geochemical analyses of soil samples to identify and characterize the influence of the hydrothermal system of Pico de Fogo, beyond its summit crater.

2. Context

Fogo volcano (Cape Verde) is the most active volcano in the eastern Atlantic, with at least 27 recorded eruptions in the last 500 years. Most of this volcanic activity occurred in the plain of Chã das Caldeiras, a ~8 km diameter horseshoe-shaped caldera with numerous cinder cones distributed along three main radial directions, also called rift zones, located in the W, NNE and SSE areas partially filling the collapse scar that affected the eastern slope of the island (Torres *et al*., 1998). At the summit crater of the main volcanic edifice (2928 m), Pico do Fogo (Figura 1), gas emissions were measured with a daily rate of ~219 t CO_2, and ~25 kg H_2S, with sulphur deposits, typical of hydrothermal activity (Dionis *et al*., 2015). At Chã das Caldeiras, recent volcanic activity produced extensive lava flow fields (Teves, 2018). The latest eruption took place in 2014-15, on an SSW-NNE 700 m-long fissure, with emission of gases, pyroclasts, and lava flows covering a total area of ~5 km^2 (Mata *et al*., 2017).

Soils in Chã das Caldeiras are thin and incipient, derived from a substrate largely composed of weakly altered pyroclastic materials, generally with a tendency towards alkalinity, low organic matter (OM) content, and poor water retention capacity, with fine ash in their matrix, as well as particles transported by masses of external air (*e.g.*, Sahara transported dust; Candeias *et al*., 2021).

3. Material and methods

A total of 65 superficial soil samples (~10 cm deep) were collected every 150 m (and every 25 m near the 2014-15 eruptive vent) 4 years after the last eruption, in the area surrounding the main volcanic edifice (Figura 1). Simultaneously, readings of self-potential (SP) and soil temperature (T) (Dumont *et al*., 2019), were taken to provide further information on the fluid circulation at the volcano (Zlotnicki and Nishida, 2003). The high input impedance Lippmann voltmeter (sensitivity: 0.1 mV; input impedance: 20 MΩ) was utilized to conduct SP measurements together with an insulated cable of 150 m length connecting a pair of non-polarizable Petiau electrodes (Petiau, 2000; Zlotnicki and Nishida, 2003). The 150 m-long profiles were drift-corrected and referred to the northwesternmost point (black star, Figura 2a). A K-type thermocouple (accuracy of ±0.1% + 0.6 ºC) was employed to measure soil temperatures, while the position of each measurement was determined with a handheld GPS receiver (accuracy <10 m). To highlight thermal anomalies associated with processes of volcanic origin, temperature data were corrected based on semidiurnal and diurnal variations.

Soil samples < 2 mm fraction were analyzed to obtain physical parameters (pH, organic matter (OM), and electrical conductivity (EC)), and geochemical characterization by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray Diffraction XRD, and for individual particles characterization" was used a Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), at GeoBioTec/University of Aveiro (Portugal). Data was subjected to multivariate statistical analysis (non-parametric Spearman correlation, and Principal Component Analysis (PCA)), using SPSS 22®. Enrichment factor and the Geoaccumulation index were calculated using the methods described by Shirani *et al*. (2020).

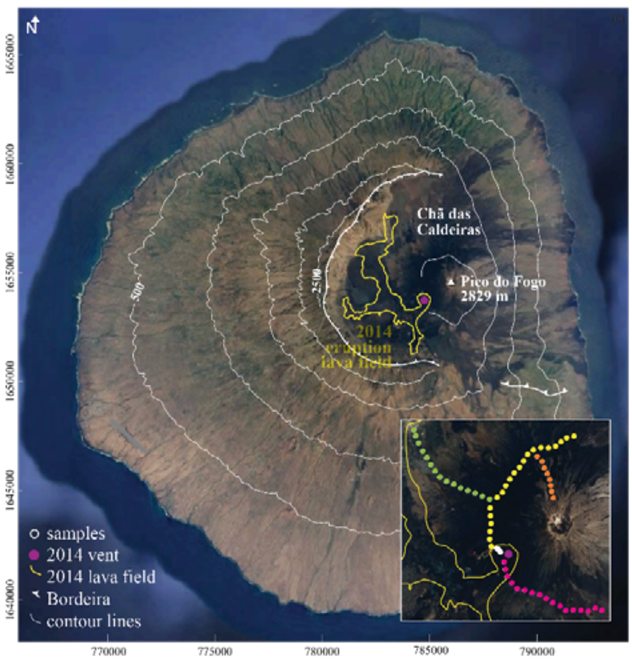

Figure 1. Fogo island with 2014 eruption vent (purple dot) and lava field (yellow line), Chã das Caldeiras, and Pico do Fogo identified. In the inset, the dots locate the 65 soil samples collected every 150 m (color by section: NW flank in green; N flanks in yellow; N slope in orange; 2014-2015 eruptive fissure in white; and S flank in pink).

Figura 1. Ilha do Fogo com identificação da erupção de 2014 (ponto rosa) e campo de lava (linha amarela), Chã das Caldeiras e Pico do Fogo. No quadrado, os pontos representam as 65 amostras de solo colhidas a cada 150 m (cor por seção: flanco NW em verde; flancos N em amarelo; declive N em laranja; fissura eruptiva 2014-2015 em branco; e flanco S em rosa).

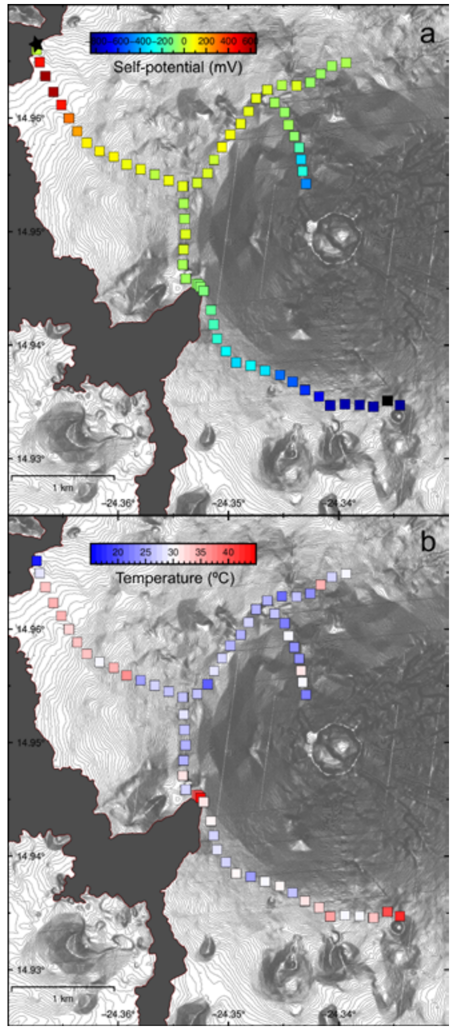

Figure 2. Self-potential (SP) (a) and temperature (b) measurements. SP values are relative to the initial measurement in Portela (black star). The 2014-2015 lava field is represented by the dark gray area.

Figura 2. Medições de Potencial Espontâneo (SP) (a) e Temperatura (b). Os valores de SP são relativos à medição inicial na Portela (estrela Negra). O campo de lava 2014-2015 é representado pela área em cinza-escuro.

4. Results and discussion

Analyzed soil samples were derived from alkaline basaltic lavas (SiO_2 < 45 %) and characterized by minerals typical of those rocks, such as clinopyroxene (*e.g.*, aegirine [$NaFe^{3+}Si_2O_6$]) and olivine (*e.g.*, forsterite [Mg_2SiO_4]). Soils exhibited an alkaline pH and a low OM content (Table 1), suggesting incipient pedogenetic processes typical of semi-arid environments which was also supported by individual particles analysis by SEM-EDS (Figura 3).

The chemical analyses (Table 1) of the soil samples show that the distribution of chemical elements, defined by similar trends of concentration, formed 4 main groups of soil samples: (a) Fe, Ca, Mn, Ti, V, with higher content located along the N volcano slope, and near the last eruption vent; (b) K, Al, Ba, Ga, Na, P, Rb, Sb, Sr, Th, U, Zn, with higher content at the S and N flanks of Pico do Fogo; (c) Mg, Cr, Cu, Ni, S, Sc, with higher content at volcano's NW and N flanks; and (d) Se, Sb, Zr, Te, Pb, with higher content along the N and S flanks of the volcano. The content in Fe and Al, important elements for the soil colloidal components,

Table 1. Physical parameters and chemical content of the soil samples.

Tabela 1. Parâmetros físicos e análise química das amostras de solo.

	minimum	maximum	median	world soils*
pH	6.9	9.1	8.1	-
EC	2.0	4.1	2.3	-
OM	0.00	0.61	0.05	-
Al	46 300	78 300	71 300	80 000
Ba	459	979	848	500
Ca	25 600	52 600	44 200	14 000
Co	28	41	33	10
Cr	18	77	41	80
Cu	44	68	57	25
Fe	63 200	85 900	76 000	35 000
Ga	15	32	23	-
K	15 400	26 200	22 700	14 000
Mg	13 600	27 900	19 900	9 000
Mn	972	1 380	1 240	530
Na	18 600	32 900	28 400	10 000
Ni	21	84	31	20
P	2 970	4 110	3 680	750
Pb	2.1	6.6	4.2	17
Rb	40	78	67	65
S	300	800	300	800
Sb	0.03	0.19	0.05	0.5
Sc	3.2	10.5	7.1	12
Se	0.1	34.5	0.8	0.3
Sr	420	1170	948	240
Te	0.006	2.050	0.056	0.006
Th	2.7	5.8	4.8	9.4
Ti	10 050	17 250	12 900	4 000
U	0.7	1.6	1.3	2.7
V	208	276	248	90
Zn	83	121	116	70
Zr	27	119	76	230

* Reimann and Caritat (1998); EC – Electrical Conductivity, in mS/cm; OM – Organic Matter, in %, and all the elements in mg/kg.

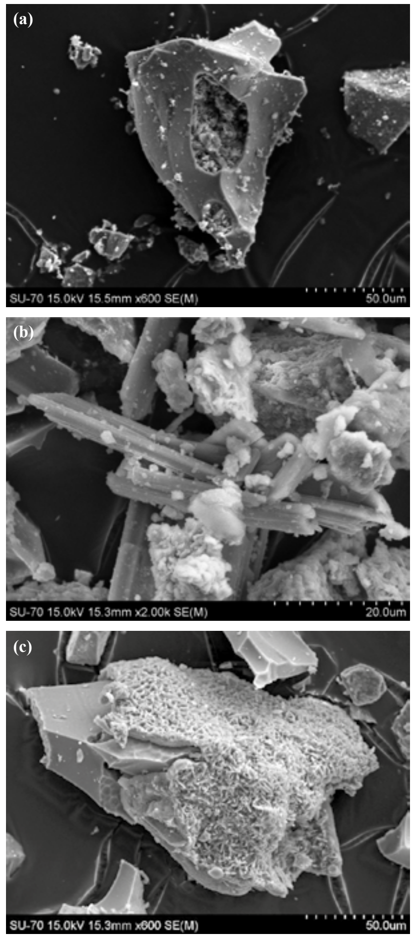

Figure 3. SEM analysis of soil individual particles: (a) an example of a particle with a mineral agglomerate enriched in Fe, S, and Ti, with angular morphology typical of magmatic fragmentation processes, showing limited or no weathering; (b) aragonite [$CaCO_3$] with minerals cluster enriched in Fe, Ti, and S; and (c) at the center, an angular fragmented particle with Al/Ca-bearing minerals deposited.

Figura 3. Análise SEM de partículas de solo: (a) exemplo de partícula com aglomerado mineral enriquecido em Fe, S e Ti, com morfologia angular típica de processos de fragmentação magmática, apresentando reduzida a inexistente meteorização; (b) aragonite [$CaCO_3$] com aglomerado de minerais enriquecidos em Fe, Ti e S; e (c) no centro, uma partícula angular fragmentada com minerais de Al/Ca depositados.

was inversely proportional to the OM content, confirming the early stage of the pedogenetic processes.

Principal component analysis (PCA) of the studied soil samples identified three principal components (PC): (a) Al, Ca, Fe, K, Na, P, and Ti (61.53 % of the variance explained), which were related to the identified mineral phases, *e.g.* augite [$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$], diopside [$CaMgSi_2O_6$], magnetite [$Fe^{2+}Fe^{3+}{}_2O_4$], abundant minerals in the study area, with significant correlation between the elements, *e.g.*, Fe/Ti (r = 0.878, $p < 0.01$ – ilmenite [$Fe^{2+}TiO_3$]); Ca/*p* (r = 0.578, $p < 0.01$ – fluorapatite [$Ca_5(PO_4)_3F$]); K/Al (r = 0.753, $p < 0.01$ – illite, leucite [$K(AlSi_2O_6)$]). Second PC, characterized by Co, Ni, Cr, and Mg (explaining 18.01 % of the variance), with metals that can be easily incorporated in Mg enriched minerals, *e.g.*, forsterite, with correlation between Mg/Cr (r = 0.608; $p < 0.01$), Mg/Ni (r = 0.544; $p < 0.01$), and Mg/Co (r = 0.282; $p < 0.05$). Third PC, with Se and Cu (8.64 % of the variance) with a Se/Cu negative correlation (r = -0.325; $p < 0.01$) that can be justified by opposing variables mobility in alkaline environment, *i.e.*, Se with high mobility and, Cu with very low mobility.

The enrichment factor (EF), in comparison to the 2014-2015 lava flows, was low (mean value of 1.02) in all elements except for Ca, Cu, Co, Fe, Na, P, and Ti (2.81), suggesting a low external enrichment of the soils, which is possibly explained by the input of Saharan dust, and aerosols produced by wildfires in continental Africa that are regularly transported to the archipelago (Guimarães, 2017). Higher EF was detected for Ca and Na, in comparison to the high content in parent lava (Mata *et al*., 2017). The Geoaccumulation index (Igeo) confirmed the EF results. Nickel was the element that presented higher content, when compared with the 2014-2015 lavas, that might be related to local anthropogenic activities.

The spatial variation of the geophysical data (Figura 2) can be summarized by examining the five areas indicated in the inset of Figura 1 (Table 2). First, the NW sector features the largest SP values with a mean value of +207 mV, and a mean temperature slightly higher than that of the whole area (Table 2, Figura 2). Such a positive SP signal may be interpreted as an upward fluid flow. This area is also characterized by soils with a pH which is slightly lower than the mean pH obtained for the whole area and with a relatively high EC. The S flank and the N ramp showed both negative SP values indicating a downward circulation of fluids. There, the physical soil properties were very similar, as for the N flank, where the soil temperatures are more stable and relatively cold compared to that on the S flank. However, the electrical behavior of the N and S flanks contrasted, as positive SP values were detected on the N volcano's side, suggesting opposite flow directions. Finally, in the sector of the last eruptive vent, higher values in soil temperature and OM content were observed associated with low pH and negative SP values.

The first-order comparison between geophysical and geochemical data suggested some correlations in the distribution of higher element concentration, soil physico-chemical properties and pattern of fluid circulation, as revealed by SP measurements (Figura 2). Specifically, two areas exhibited distinctive features: 1) in the sector of the 2014-2015 eruptive fissure where anomalies were predominantly observed in the soil properties, and 2) in the NW area, where anomalies were predominantly detected in the fluid circulation (Table 2, Figura 2). An in-depth analysis of these cross-disciplinary data sets is currently being conducted to unravel the sources of spatial variations in soil properties and composition, and, thus, better decrypt the fluid circulation and the hydrothermal system of Pico do Fogo volcano.

5. Conclusions

The geochemical analyses of soil samples, together with self-potential and temperature data, collected in the direct vicinity of Pico do Fogo, provide new insights on the surface expression of the hydrothermal activity at the scale of the volcano edifice. While thermal and electrical measurements contributed to characterize the fluid motion, soil physico-chemical properties and mineralogy will shed light on its nature, and on the intensity of hydrothermal phenomena as revealed by the soil analyses. These preliminary results revealed how important is the integration of cross-disciplinary data to unravel complex processes involving both physical and chemical phenomena such as hydrothermal circulation.

Table 2. Self-potential, temperature variation, pH, electrical conductivity, and organic matter quantified for the different areas.

Tabela 2. Potencial espontâneo, variação de temperatura, pH, condutividade elétrica e matéria orgânica nas diferentes áreas.

Area	SP	ΔT	pH	EC	OM
NW flank	207.4	30.2	7.7	2.5	0.32
Fissure	-81.2	38.5	5.8	2.3	1.52
S flank	-525.8	31.3	8.0	2.3	0.11
N flank	7.5	26.8	8.3	2.3	0.06
N ramp	-181.4	26.0	8.2	2.3	0.07
all	-114.6	29.4	7.9	2.3	0.22

SP – self-potential, in mV; ΔT – temperature variation, in ºC; EC – Electrical Conductivity, in mS/cm; and, OM – Organic Matter, in %.

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