Geochemistry and Fe speciation in active volcanic environments – the case of Fogo Island, Cape Verde

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Abstract. Topsoils developed in different geological formations/ages, and the top layer of the lava flow from the most recent eruption (2014/2015) of Fogo Island (Cape Verde archipelago), were studied. The specific objectives of this work are: i) to estimate the REE contents and patterns in the whole sample of topsoils developed on different geological formations/ages and their correlation with the iron speciation; and ii) to study the top layer of a lava flow from the most recent eruption after two years of exposure. REE contents are in general higher in the topsoils of the pre-caldera than in those developed on the post-caldera formation, particularly the light REE probably due to their incorporation into hematite. Positive Eu anomalies found in recent topsoils suggest the existence of hydrothermal processes with intrusion of hot fluids with higher concentration of Eu^{2+}. In the top layer of the lava flow of the most recent eruption, Fe is incorporated in pyroxenes and iron oxides (magnetite and/or maghemite). This study can be a benchmark for further knowledge of the chemical evolution and weathering rate in semi-arid climate of Fogo Island.

1 Introduction

Volcanic soils contain an abundance of iron and trace elements, being very fertile and with exceptional chemical properties, resulting from weathering of the parent rock and from the climate conditions associated [1, 2]. Among the crystalline iron (hydro)oxides, hematite is one of the most abundant minerals in well-drained soil, while maghemite and magnetite may exist in poorly drained soils [3 and references herein]. After release of Fe from primary minerals, under aerobic conditions and with pH values ranging from 5 to 8, Fe^{2+} is readily oxidized [3]. This behaviour was clearly observed in Fogo Island (Cape Verde),

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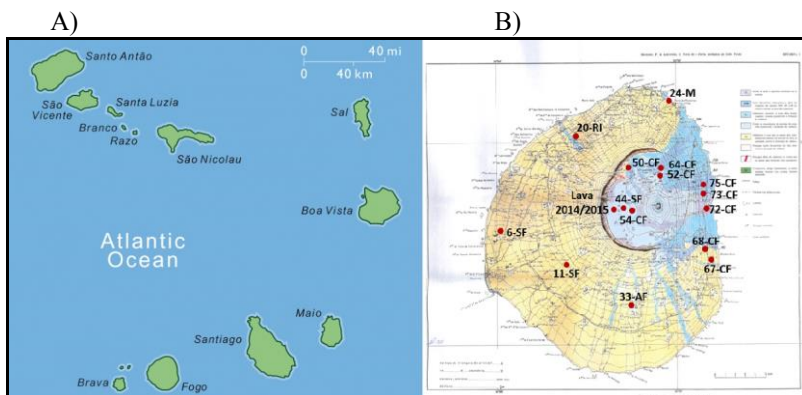* Corresponding author: iprudenc@ctn.tecnico.ulisboa.pt

where under a semi-arid climate, oxidation is the major chemical weathering process [4]. Other chemical elements abundances in soils, like the rare earth elements (REE), may vary significantly with the type of parent rock or source area. Primary minerals like apatite are enriched in light REE (LREE) while zircon has higher amounts of heavy REE (HREE) [5, 6].

Fogo Island is located in the south-western part of Cape Verde archipelago (15˚N, 24.5˚W), around 800 km far from Africa coast (Fig.1A). The origin of the archipelago is related to the hotspot magmatism, which involves predominantly alkalic silica-undersaturated melts of basanitic to tephritic composition. The volcanic rocks of Fogo include mainly three main stratigraphic units: a) a carbonatite unit exposed in fluvial valleys near S. Filipe and assumed as the oldest rocks of the island, b) a major volcanic sequence related to the sub-aerial shield-building of the island volcano (nephelinites and associated lavas with layers of scoria or tuffs, previous to the caldera formation), and c) a post caldera sequence including several historic eruptions [7, 8]. Fogo is one of the youngest islands (≈ 5 Ma), and the only volcanic active island in Cape Verde [9].

The main goals of this work are: i) to estimate the REE contents and patterns in the whole sample (ϕ < 2 mm) of topsoils developed on different geological formations/ages and their correlation with the iron speciation; and ii) to study the top layer of a lava flow from the most recent eruption (2014/2015), after two years of exposure, to be used as a benchmark for further understanding of the chemical evolution and weathering rate. This study is also a contribution to the construction of the database for the Geochemical Atlas of the Fogo Island.

2 Materials and methods

Field work was performed in Fogo Island between 2009/2010 and samples of the surficial layer (0-20 cm) of soils developed on different geological and geographical contexts were collected: five topsoils developed in rocks of the pre-caldera formation - one carbonatite, three nephelinites and one limburgite; and 12 topsoils from rocks of the post-caldera formation – eight lavas and pyroclasts from historic eruptions, one pre-historic pyroclast (prior to 1721) and three deposits (torrential or lahar) (Fig.1B). Two samples of the top layer of the lava flow (UTM: X=791,200; Y=1,653,779) from most recent eruption were collected in 2017: i) Lava-A of a grey-brownish colour, and ii) Lava-B of blackish colour.

Fig. 1. A) Cape Verde archipelago (http://hispanopress.blogspot.com/2015/04/islas-de-cabo-verde-mapas-geograficos.html); B) Sampling location on the Fogo Island (Cape Verde), adapted from [10].

The whole samples were obtained by sieving through a 2 mm nylon mesh sieve, dried, and ground in agate mortars for chemical analysis. The Fe and REE total contents were

obtained by instrumental neutron activation analysis (INAA), using two reference materials from the Institute of Geophysical and Geochemical Exploration (IGGE). Reference values were taken from tabulated data [11]. Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). The irradiations were performed in the core grid of the Portuguese Research Reactor (CTN/IST, Bobadela) [12], at a thermal flux of 3.96×10^{12} n cm^{-2} s^{-1}; $\phi_{th}/\phi_{epi} = 96.8$; $\phi_{th}/\phi_{fast} = 29.8$. More details of the analytical method may be found elsewhere [13].

The mineralogical composition of the two samples of the top layer of the lava flow was obtained by X-ray diffraction (XRD) on non-oriented aggregates.

The ^{57}Fe Mössbauer measurements were recorded at 295 K and 4.2 K in transmission mode. Details may be found in ref. [4]. The spectra were fitted to Lorentzian lines using a non-linear least-square method [14].

3 Results and discussion

The chemical contents of Fe and REE are shown in Table 1. It should be noted that the iron concentration data for the topsoils were already reported [4].

Table 1. Chemical contents of Fe (% w/w) and REE (mg/kg) obtained by INAA for the topsoils, and the top layer of the lava flow of 2014/2015 from Fogo Island (Cape Verde).

		Sample reference	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Fe$_2$O$_3$T *
Topsoils	**Pre-caldera formation**	**6-SF**	105	219	111	18.2	5.95	2.21	9.34	4.49	0.410	8.46
		11-SF	155	267	149	24.6	7.37	2.29	13.8	5.49	0.603	11.9
		20-RI	80.0	153	82.3	16.9	5.02	1.75	9.81	3.09	0.425	12.9
		33-AF	89.7	174	103	17.2	5.23	1.53	9.03	3.16	0.395	14.4
		67-CF	58.3	99.5	55.1	11.6	3.40	1.23	6.51	2.70	0.310	9.93
	Post-caldera formation	**72-CF**	51.5	107	64.0	9.91	3.24	1.17	5.15	2.53	0.293	9.79
		73-CF	55.1	115	65.0	11.4	3.18	1.13	5.15	2.51	0.279	8.53
		24-M	55.3	119	54.2	11.8	3.50	1.31	6.10	2.54	0.287	9.23
		44-CF	67.0	151	73.6	8.86	3.70	1.36	6.16	3.30	0.366	6.91
		50-SF	55.6	126	62.5	8.77	3.65	1.25	6.22	2.82	0.313	8.95
		52-CF	55.0	121	61.9	8.77	3.54	1.43	6.59	2.79	0.302	9.37
		54-CF	55.4	126	39.3	8.70	3.60	1.43	7.15	2.86	0.420	9.02
		64-CF	57.0	103	61.8	11.2	3.39	1.15	5.71	2.65	0.288	9.37
		68-CF	58.1	111	62.3	10.8	3.34	1.25	5.70	2.67	0.292	8.74
		75-CF	55.9	113	63.0	10.9	3.03	1.19	5.10	2.48	0.318	7.69
Top layer of lava of 2014/2015		**Lava-A**	59.4	131	61.0	9.50	2.80	0.800	3.90	2.60	0.250	9.08
		Lava-B	59.2	121	60.0	9.20	2.80	0.740	3.60	2.20	0.180	8.52

* data from [4].

A previous detailed Fe speciation study [4] showed that oxidation is the major weathering mechanism, and magnetite is gradually oxidized to hematite. In addition, the most oxidized topsoils are the oldest ones from the pre-caldera formation when compared to the post-caldera topsoils.

The REE contents are in general higher in the topsoils developed on the pre-caldera than in those developed on the post-caldera formation, particularly the LREE, which can be due to higher contents in the parent rock and/or a higher weathering degree. The REE contents increase with weathering was found previously in Fogo, particularly the LREE in this semi-arid environment which may be partially explained by their incorporation in hematite [15]. In some of the most recent topsoils (Fig.2A), such as those developed on lava and pyroclasts of the 1951 and 1995 eruptions, positive Eu anomalies are observed, suggesting the existence of hydrothermal processes involving hot fluids with high REE contents [16]. This behaviour was already observed on volcanic conduits of this Island [17] and was explained by the higher mobility of Eu^{2+} in the pores of the materials when compared to Eu^{3+}. The REE patterns of the topsoils developed on deposits (Fig.2B) contemporaneous to post-caldera formation, and of both samples of the top layer of the lava of 2014/2015 (Fig.2C) show the same trend of the topsoils of this formation.

The results obtained by XRD of both samples of the top layer of lava from 2014/2015 eruption show that pyroxenes are dominant; alkali feldspars occur in trace amounts in both samples. Mössbauer results show that a large fraction of the Fe is present as Fe^{2+} in a vitreous phase (Table 2). In Lava-A, magnetite and maghemite are observed, both bulk and nano-sized, while in Lava-B only nano-sized maghemite is detected. Fe in the silicates structure, mainly pyroxenes, is mostly in the 2+ oxidation state. The Fe oxidation degree in the whole sample is higher in Lava-A than in Lava-B mainly due to the highest amount of vitreous phase in the latter.

Table 2. Fe oxidation degree and distribution in different mineral phases obtained by Mössbauer spectroscopy for the samples of the top layer of lava flow of 2014/2015 eruption from Fogo Island (Cape Verde).

	% Fe^{3+} whole sample	%Fe in oxides (nso and bulk)	%Fe in nso*	%Fe^{3+} silicate	%Fe^{2+} silicate	%Fe in glass
Lava-A	40	42	20	5	15	38
Lava-B	26	23	23	3	16	58

*nso nano-sized Fe^{3+} oxides.
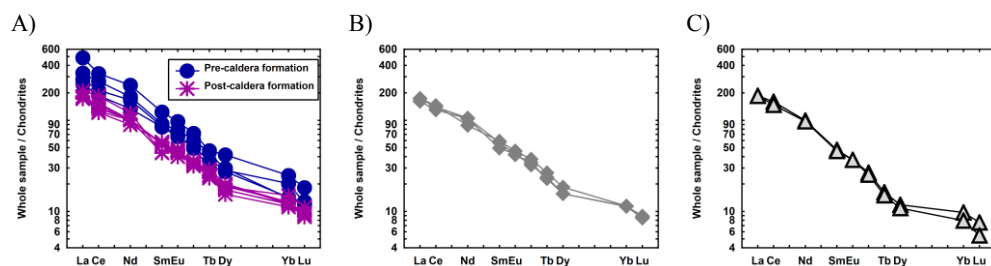
Fig. 2. REE patterns of the whole samples relative to chondrites of: A) topsoils developed on the pre-caldera and post-caldera formations, B) topsoils developed on deposits (de/lahar) contemporaneous to post-caldera formation, and C) top layer of lava flow of the most recent eruption of Fogo Island (Cape Verde).

The study here presented of the top layer of the lava flow of the most recent eruption occurred in Fogo Island should be a reference and can be used in future studies for the evaluation of the weathering rate and the chemical evolution of volcanic materials in the semi-arid climate of Cape Verde.

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