Geochemistry and mineralogy of volcanic soils from Ocean Fogo island (Cape Verde)

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Abstract
The chemical and mineralogical study of topsoils (< 2mm) from the ocean volcanic island of Fogo was performed aiming the establishment of geochemical patterns of soils, especially the trace element distribution. The morphology of this semi-arid island corresponds to a conic volcano edifice, with three main stratigraphic units: (I) a carbonatite unit, (II) a major volcanic sequence (nephelinites and associated lavas, scoria and tuffs), and (III) a post caldera sequence including several historic eruptions. The chemical and mineralogical analyses were done using neutron activation analysis and X-ray diffraction. The topsoil developed on carbonatites is clearly distinguished by high contents of K, Rb, Cs, W, Th and rare earth elements (REE). The soils from unit II have a similar chemical composition, except one sample that presents higher REE, Fe, As, Cs, Ba, Zr, Hf, Ta and Th contents. The main mineral compounds identified in Fogo topsoils are pyroxenes, feldsphathoids, magnetite-maghemite, titanomagnetite, zeolites and phyllosilicates. The soil developed in carbonatites shows a distinct mineralogical association, with calcite, mica, phyllosilicates, and feldspars. Quartz and mica are in general found in the studied soils of this volcanic island, derived most probably from particulate deposition from the atmosphere transported by wind from North Africa (Sahara).

Key Words
Soil, Fogo island, trace elements, REE, mineralogy, atmospheric deposition

Introduction
The island of Fogo (15.0N, 24.5W) is located in the south-western part of Cape Verde and is the fourth bigger island (476 km^2 area) of this archipelago (Figure1). This is a relatively simple island-volcano, corresponding practically to an active volcano with a maximum altitude of 2829 m. The island is characterized by a semi-arid climate, raining mainly between July and October. The average annual temperature of Fogo island is about 25ºC. However, in Chã das Caldeiras (See Figure 1b) in December and January the temperature decreases to 0ºC (Mota Gomes, 2006).

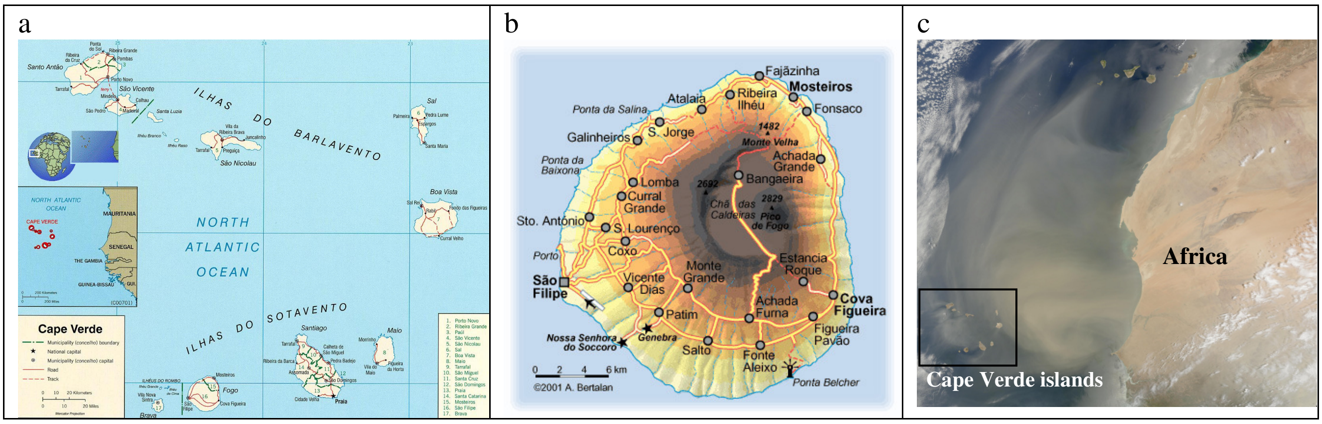

Figure 1. a- Location of Fogo island (www.okcapeverde.com/Cape-Verde-Islands-Map.jpg); b- Fogo island map; and c- NASA image SeaWIFS collected in May2007 – dust from North Africa often blows across de Atlantic in to Cape Verde islands (http://oceancolor.gsfc.nasa.gov/cgi/image_archive.cgi?c=DUST).

Three main stratigraphic units include the volcanic rocks of Fogo: (I) a carbonatite unit exposed in fluvial valleys near S. Filipe and assumed by most authors as the oldest rocks of the island, (II) 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 (III) a post caldera sequence including several historic eruptions (Madeira *et al*., 2005; Madeira and Brum da Silveira, 2005).
In this work a detailed chemical characterization (28 trace and major elements) of topsoils collected on the west slope of Fogo Island (Figure 2) in the two first units (carbonatite and sub-aerial shield-building), was obtained by neutron activation analysis. A mineralogical study was also done by X-ray diffraction. The main objective of this work is the establishment of geochemical patterns of topsoils derived by weathering of different types of volcanic rocks, particularly trace elements distribution. The correlation of the chemical composition with the mineral phases is also done. The evaluation of atmospheric deposition is also a major goal (Derry and Chadwick, 2007), since a contribution of fine materials transported by Trade Winds from North Africa (Sahara) is expected (see Figure 1c). This work is being done in the framework of a larger project compiling a geochemical atlas of low/medium density of Cape Verde islands.

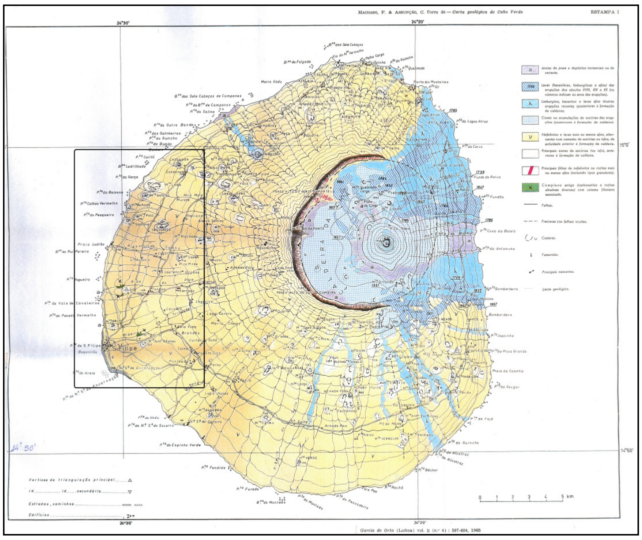

Figure 2. Geological map of Fogo island with the indication of the studied area (black rectangle) (Machado F, Assunção C. Torre de, Carta Geológica de Cabo Verde, 1965)

Methods

Sample collection and analytical methods

A field work was done in the Fogo island in October of 2009 in order to select and collect topsoils (regolith). In depth coring was done to collect surface (0-25 cm) samples. The whole sample (<2mm) was obtained by sieving and then ground in agate mortar.

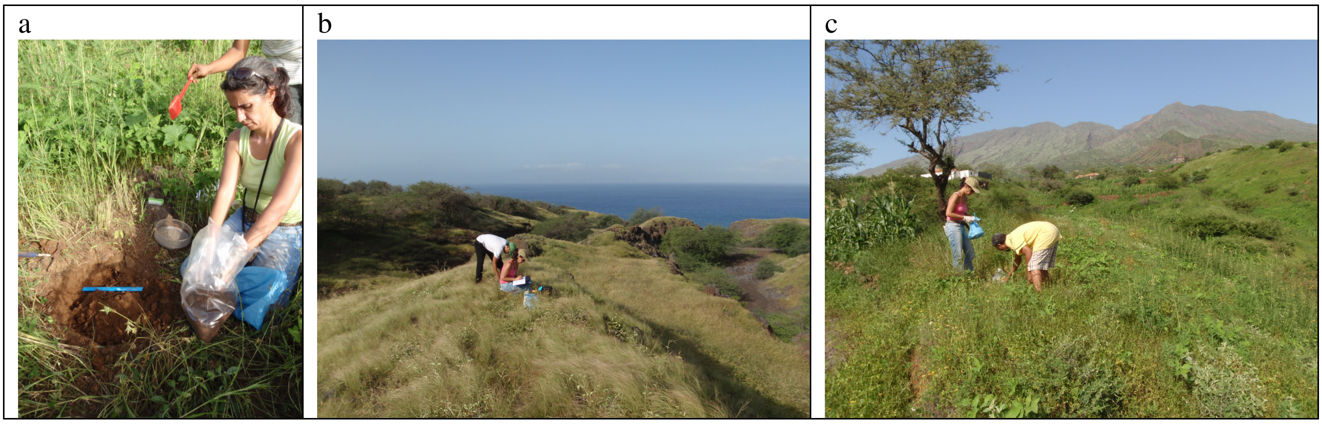

Figure 3. a- Sampling a topsoil of unit II; b and c- sampling locations of inter-fluvial areas of unit II.

The mineralogical composition of whole samples was obtained by X-ray diffraction (non-oriented aggregates). The neutron activation analysis was applied for the determination of chemical contents in the whole sample of topsoils. Reference samples of soil (GSD9) and sediment (GSS4) from the IGGE from the People's Republic of China were used as standards. The irradiation of the samples and standards were done in the core grid of the Portuguese Research Reactor. The chemical contents of Na, K, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th e U were obtained with a good precision and accuracy (in general <5%) (Gouveia and Prudêncio, 2000).

Results

The chemical results obtained so far show that the soil developed on carbonatites (unit I sample) is easily distinguished by higher contents of rare earth elements (REE), particularly the light and middle ones, K (2.17% K_2O), Rb (222 µg/g), Cs (1.65 µg/g), W (4.56 µg/g), and Th (9.17 µg/g) and lower contents of Sc (12 µg/g) and Cr (41.1 µg/g). Also a significant negative Ce anomaly was found in the carbonatite soil (Figure 4).

Among the soils developed in unit II (volcanic sequence related to the sub-aerial shield-building of the island volcano), most of the samples already analysed present a similar geochemical pattern (called unit II-a in the present work), except for one sample collected in the north-western part of the studied area (unit II-b sample). Concerning the REE, unit II-b presents higher contents of REE, especially light and middle REE (see Figure 4a), and higher contents of Fe (19.1 % Fe_2O_3T), As (3.56 µg/g), Cs (1.45 µg/g), Ba (913 µg/g), Zr (573 µg/g), Hf (10.1 µg/g), Ta (9.12 µg/g) and Th (8.87 µg/g).

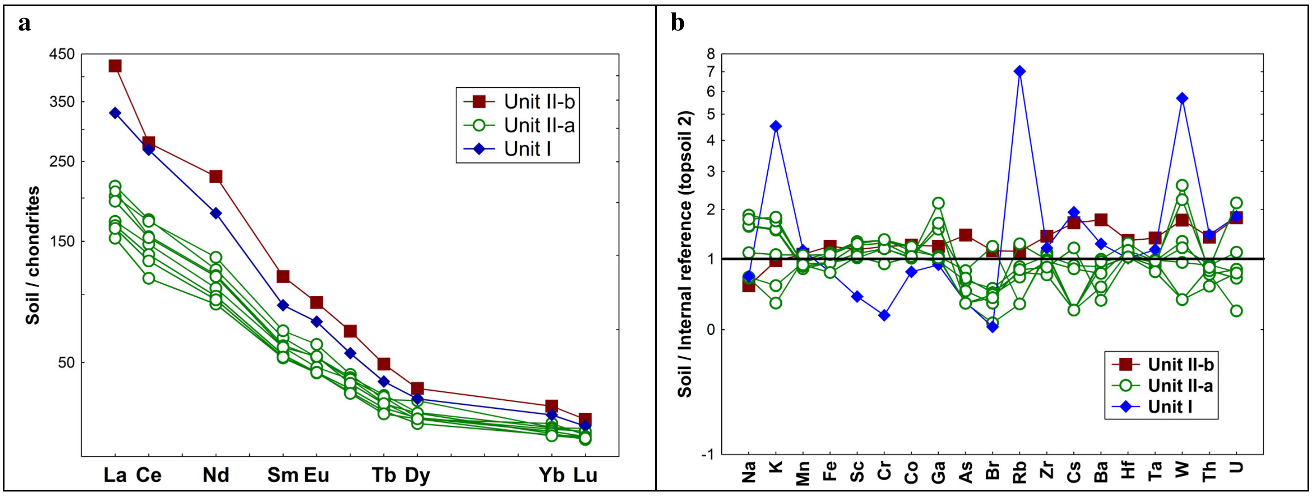

Figure 4. a- Chondrites-normalized patterns of REE of the whole sample (<2mm) of topsoils from Fogo island (chondrites values of Anders and Grevesse (1989) times 1.36, obtained by Korotev (1996)); b- chemical contents in topsoils from Fogo island relative to an internal reference sample (topsoil 2 belonging to the unit II).

In the topsoils of unit II-a, the higher chemical contents variations were found for Na, K, Ga, Br, W and U (Figure 4b). The REE fractionation observed is mainly due to a higher variation of the light REE contents (see Figure 4a). High contents of Br are found (up to 193 µg/g), which has been already found in other Atlantic islands of Azores (Vieira *et al.*, 2004).

The mineralogical study by XRD point to the existence of a significant vitreous component, since low crystalinity was revealed by the diffractograms obtained, as could be expected for these volcanic soils. Among the mineral compounds identified by XRD in Fogo topsoils of unit II, pyroxenes, feldsphathoids, magnetite-maghemite, titanomagnetite, and zeolites were found. The soil derived by weathering of carbonatites is mainly composed of calcite, mica, phyllosilicates, and feldspars; traces of zircon and apatite were also detected.

It should be noted that different proportions of quartz and mica were also detected in these soils, which can be derived from atmospheric deposition of grains transported by wind from North Africa (see Figure 1 iii), as already found in the Canary archipelago (Mizota and Matsuhisa, 1995).

Conclusion
The results obtained so far show that topsoils of the ocean Fogo island present significant chemical variations mainly in the concentrations of REE (particularly the light and middle REE), K, Sc, Cr, Fe, As, Br, Rb, Zr, Cs, Ba, Hf, Ta, W, Th and U. The differences found are related with the parent rock, topography and the geographic location. Bromine may have been added to the soils by wet deposition (ocean origin), explaining the high contents of this volatile element found in some soils.
Despite the reduced number of samples already analysed, the chemical and mineralogical composition appears to contribute for the characterization and differentiation of topsoils of the Fogo island (among and within the same geological unit). Quartz and mica found in the topsoils of this ocean volcanic island may be transported from North Africa (Sahara) deserts by Trade Winds. Chemical and mineralogical characterization of a larger number of samples of different lithology and geographic locations of the island is being undertaken.

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