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Extrusive carbonatite outcrops – A source of chemical elements imbalance in topsoils of oceanic volcanic islands

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ABSTRACT

Extrusive carbonatite ash tuff (Tantum) and spatter (Monte Miranda) deposits, and topsoils (incipient and shallow) from both sites of Brava Island (Cape Verde archipelago) were studied by neutron activation analysis, X-ray diffraction and Mössbauer spectroscopy. The ash tuff deposit near Tantum, here reported for the first time, corresponds to an extrusive calciocarbonatite with high W, Th, U and REE contents and a positive Eu anomaly. Similar REE patterns and W concentrations were also found in the spatter deposit of Monte Miranda. Magnetite is the major iron containing phase in both extrusive carbonatite deposits. High W and REE concentrations associated with the presence of calcite prevail in topsoils with extrusive carbonatite influence. In the topsoil developed on extrusive carbonatite ashes, magnetite is well preserved particularly in the coarser fractions probably due to the recent age of the parent material associated with the semi-arid climate of the island; a significant chemical heterogeneity of the whole samples as well as of the different size fractions of these topsoils was found, with an enrichment of Co, Zn, Ga, As, Br, Rb, Ce, and particularly Sb and W in the clay-size fraction, which may be relevant for the study of environmental health issues in Brava Island.

1. Introduction

Carbonatites are magmatic rocks with > 50% volume of carbonate minerals, characterized by high contents of Sr, Ba, P and light rare earth elements. They can be divided into calcio-, dolomitic- or magnesio-, ankeritic- and natro- carbonatites, according to the dominant carbonate mineral (e.g. Le Maitre, 2002). This type of rock usually occurs within stable, continental intraplate settings, more than half of them located in Africa (Jones et al., 2013). Their occurrence has been related to mantle plumes and large igneous provinces (Bell and Simonetti, 2010; Ernst and Bell, 2010). Intrusive types are dominant with volcanic outcrops representing only 10% of the known occurrences worldwide (Woolley and Church, 2005).

Oceanic carbonatites are extremely rare and their occurrence was first reported by Assunção et al. (1965) in Cape Verde, and by Fúster et al. (1968) and Allègre et al. (1971) in Fuerteventura (Canary Islands). However, Bebiano (1932) had already mentioned "calcareous dikes" and "calcareous masses of volcanic origin" in S. Vicente Island (Cape Verde). As far as we know, besides Cape Verde and Canary Islands no other occurrences of carbonatite outcrops in oceanic environments have been reported, although the occurrence of mantle metasomatism envolving carbonatite melts has been referred for Kerguelen (Mattielli et al., 2002) and Madeira Island (Mata et al., 1999).

In the Cape Verde islands calcio- to magnesio-carbonatites occur on 6 out of the 10 islands, and on the islets near Brava, and have been the subject of numerous studies (e.g., Allègre et al., 1971; De Ignacio et al., 2012; Doucelance et al., 2010; Jorgensen and Holm, 2002; Kogarko, 1993; Mata et al., 2010; Mourão et al., 2010, 2012a, 2012b). In this archipelago, intrusive carbonatites are clearly dominant, and several outcrops of this type of rock were mapped by Machado et al. (1968) within the basal complexes of several islands, while the first reference to extrusive carbonatite deposits was presented by Silva et al. (1981) in Santiago Island.

The occurrence of extrusive carbonatites in Brava Island was briefly mentioned in abstracts published by Tuberville et al. (1987) and Peterson et al. (1989). Later, Hoernle et al. (2002) described one occurrence at Cachaço in southern Brava. More recently, Mourão et al.

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(2010) and Madeira et al. (2010) reported a more complete study of extrusive carbonatite outcrops corresponding to, at least, five eruptions and presenting a wide geographical dispersion on Brava Island. As reported by these authors, most of these extrusive carbonatitic formations are calciocarbonatites (according to the chemical systematics of Woolley and Kempe, 1989) and correspond to pyroclastic rocks, comprising magmatic and/or phreatomagmatic ash and lapilli fall deposits, and one pyroclastic flow. These carbonatitic eruptions are Quaternary in age and correspond to some of the younger volcanic events in Brava Island.

The semi-arid climate of Cape Verde archipelago and the rough topography of the landscape, with evidence of surface instability and recent erosion, originate incipient soils with low to moderate degree of weathering and development. The Geochemical Atlas of these islands using the chemical composition of topsoils (0–20 cm depth) is being done according to the recommendations of Darnley et al. (1995). Within this frame, a previous work performed on Brava topsoils (Marques et al., 2016) revealed that significant variations in chemical contents occur within the same geological unit, along with a chemical heterogeneity of the topsoils. High contents of Mn, Co, Ga, Ba, La, Ce, Nd, Sm, Eu, Tb, Ta, W, Th and U were observed in topsoils derived from carbonatites and phonolites; rare earth elements (REE) and W, as well as the predominance of low oxidized magnetite, appear to be good fingerprints for extrusive carbonatite outcrops. These features justify a deeper research of the previously identified topsoils by Marques et al. (2016) from Brava Island with extrusive carbonatite influence (5-BRV and 26-BRV samples). In this way further sampling of extrusive carbonatite outcrops near the identified topsoils was performed on: (a) one ash tuff deposit located at Tantum (reported for the first time in this work) and (b) the remains of a small hornito or spatter deposit near Monte Miranda (already referred by Mourão et al., 2010). A detailed compositional study was done by means of instrumental neutron activation analysis, Mössbauer spectroscopy and X-ray diffraction.

The specific objectives of the present work are: (a) the report of a newly found extrusive carbonatite outcrop near Tantum (Brava Island); and (b) the chemical and mineralogical characterization, and the iron speciation of extrusive carbonatites, and of different size fractions of the Tantum and Monte Miranda incipient topsoils (0-20 cm depth). This work is therefore a contribution for a more complete knowledge of: (i) rare oceanic extrusive carbonatite outcrops; (ii) the Brava extrusive carbonatites, which crop out in a wide geographical dispersion on the island; and (iii) the evaluation of the carbonatite influence on the imbalance of chemical elements in topsoils in the semi-arid environment of the Cape Verde archipelago.

2. Study area

Brava is a small semi-arid island (64 km^2) located on the south-western tip of the Cape Verde archipelago, in the NE–SW alignment formed together with Maio, Santiago and Fogo (Fig. 1). The exposed part of the island is formed by an older basement composed of the submarine volcanic edifice, comprising pillow lavas, pillow breccias and hyaloclastites of nephelinite/ankaramite composition, intruded by an alkaline-carbonatite complex, both of which are unconformably covered by younger sub-aerial volcanic deposits of dominant phonolitic composition (Madeira et al., 2010). These sequences led to the definition of three major volcano-stratigraphic units: (i) the older Lower Unit (2 to 3 Ma), composed of an uplifted seamount sequence representing the upper part of the submarine edifice precursor of island emergence; (ii) Middle Unit (1.8 to 1.3 Ma) corresponding to exhumed magma chambers forming a subvolcanic plutonic complex (including syenites, pyroxenites, ijolites and carbonatites), intruded into the Lower Unit; and (iii) Upper Unit (< 0.25 Ma), the younger volcanic sequence dominated by products of phonolite volcanism (characterized by phreatomagmatic and plinian pyroclastic deposits and by domes and lava flows) but also including small volumes of mafic (nephelinitic) and carbonatitic extrusions, standing on an important erosional discontinuity that truncates the older basement (Lower and Middle units) (Madeira et al., 2010; Mourão et al., 2010).

Extrusive carbonatites exposed within the Upper Unit constitute the focus of this contribution. At least 20 small outcrops of dark-brown to blackish extrusive carbonatites were found by Mourão et al. (2010) in three areas of Brava Island: in the NE around Nova Sintra, in the SW near Campo Baixo, and in the south around Cachaço and Morro das Pedras. All extrusive carbonatites were deposited at or near the top of the younger volcanic sequence. Most outcrops are made up of pyroclastic formations, comprising magmatic and/or phreatomagmatic ash and lapilli fall deposits, one pyroclastic flow, and a feeder dyke; most deposits contain abundant lithic fragments of phonolite and occasionally other lithologies.

3. Experimental

3.1. Sampling, materials and methods

Fieldwork was performed in 2013 in Brava Island, Cape Verde archipelago (see Fig.1), for the sampling of extrusive carbonatites outcrops and the surface layer of soil (0–20 cm depth), herein referred as topsoil. Field observations show an incipient pedogenesis of these shallow volcanic soils (≈ 30 cm depth).

Carbonatites were collected from two different sites: (a) near Tantum - a newly found outcrop of an ash fall deposit (5C–BRV) and the topsoil developed on it (5-BRV, Tantum topsoil) (UTM: X = 742,789 m, Y = 1,641,105 m), also with contribution of phonolite pyroclasts from the slope above, and (b) close to Monte Miranda (south of Cachaço) – a proximal spatter rampart (26R–BRV) and an adjacent ash-derived topsoil (26-BRV T, Monte Miranda topsoil) (UTM: X = 746,947 m, Y = 1,640,105 m) already referred by Mourão et al. (2010) (Figs. 2 and 3).

The topsoils samples were collected as follows: circa 2 kg was collected and sifted on-site by hand through a 20 cm diameter nylon sieve with a mesh size of 2 mm into polyethylene bags for transport. It should be noted that these topsoils consist of fine particles smaller than 2 mm in diameter. In the laboratory the samples were dried at 30 °C; samples were mixed and sieved again through a 2 mm nylon sieve (whole sample). After a repeated mixing procedure, samples were quartered by hand. Two portions (circa 100 g each) were separated for analysis: (i) sample T - to be ground and analyzed to obtain the total chemical and mineralogical composition, and (ii) sample A - for grain size fractions separation, weight and analysis (Marques et al., 2011). Two grain size fractions of sample A were obtained by wet sieving: the $\phi > 50$ μm fraction (coarse), and the $\phi < 50$ μm fraction (fine) using deionized water (nylon mesh). This fine fraction was then used to obtain the $\phi < 2$ μm fraction (clay-size) by sedimentation according to Stokes' law (Moore and Reynolds, 1997), after dispersion with sodium hexametaphosphate (1%).

Trace, minor and major elements concentrations of extrusive carbonatites (ash tuff deposit and spatter rampart deposit), as well as of the whole samples and the selected fractions of the topsoils were determined by instrumental neutron activation analysis (INAA). Two reference materials were used in the evaluation of elemental concentrations by INAA: soil GSS-4 and sediment GSD-9 from the Institute of Geophysical and Geochemical Prospecting (IGGE). Reference values were taken from data tabulated by Govindaraju (1994). The samples and standards were prepared for analysis by weighing 200–300 mg of powder into cleaned high-density polyethylene vials. Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). Short and long irradiations were performed in the core grid of the Portuguese Research Reactor (CTN/IST, at Bobadela) (Fernandes et al., 2010) at a thermal flux of 3.96×10^{12} n cm^{-2} s^{-1}; $\phi_{th}/\phi_{epi} = 96.8$; $\phi_{th}/\phi_{fast} = 29.8$. Two γ-ray spectrometers were used: (1) one consisting of a 150 cm^3 coaxial Ge