

Chemical element accumulation in tree bark grown in volcanic soils of Cape Verde—a first biomonitoring of Fogo Island

Rosa Marques^{1,2} · Maria Isabel Prudêncio^{1,2} · Maria do Carmo Freitas¹ ·
Maria Isabel Dias^{1,2} · Fernando Rocha^{2,3}

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Abstract Barks from *Prosopis juliflora* (acacia) were collected in 12 sites of different geological contexts over the volcanic Fogo Island (Cape Verde). Elemental contents of Ba, Br, Co, Cr, Fe, K, Na, Zn and some rare earth elements (REE)—La, Ce, Sm, Eu, Tb, Yb, and Lu, were obtained for biological samples and topsoils by using k_0 -standardized and comparative method of instrumental neutron activation analysis (INAA), aiming the evaluation of chemical elements uptake by acacia bark. This first biomonitoring study of Fogo Island showed that, in general, significant accumulations of trace elements present in high amounts in these soils occur. This can be partially explained by the semi-arid climate with a consequent bio-availability of chemical elements when rain drops fall in this non-polluted environment. REE enrichment factors (EFs) increase with the decrease of ionic radius. Heavy REE (HREE) are significantly enriched in bark, which agrees with their release after the primary minerals breakdown and the formation of more soluble compounds than the other REE, and uptake by plants. Among the potential harmful chemical elements, Cr appears to be partially retained in nanoparticles of iron oxides. The high EFs

found in tree barks of Fogo Island are certainly of geogenic origin rather than anthropogenic input since industry and the use of fertilizers is scarce.

Keywords Biomonitoring · Bark · Trace elements · REE · Volcanic soils · Fogo Island · INAA

Introduction

Among the chemical elements that occur in terrestrial ecosystems, some of them are present as trace elements in soils (<0.1 wt%), resulting from processes such as chemical weathering of the parent material, volcanic eruptions, and/or forest fires. The main active agents in weathering are water, carbon dioxide, and oxygen. The weathering process is slow and continuous, producing dilute solutions of trace elements that are transported into the groundwater and eventually into the rivers, and then to the ocean, when rainfall and drainage are adequate. In regions of limited rainfall or poor drainage, the products of weathering accumulate locally (Bañuelos and Ajwa 1999). Trace elements occur incorporated in primary and secondary minerals, and their concentrations in soils reflect the nature of the parent material, climate, and drainage conditions (Förstner 1995). The accumulation of these elements in surface soils is due to their complexation by organic material (adsorption), as a result of cycling through vegetation or atmospheric deposition. The behavior of some trace elements in soils can be very complex because they can occur in different oxidation states, being soluble, exchangeable, adsorbed, or co-precipitated with carbonates, sulfides, phosphates, and hydroxides (Bañuelos and Ajwa 1999). The availability of trace elements in soils may result in bigger uptakes by plants, which presents a health risk to wildlife, and

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✉ Rosa Marques
rmarques@ctn.ist.utl.pt

¹ Centro de Ciências e Tecnologias Nucleares (C2TN), IST, Universidade de Lisboa, Estrada Nacional 10 (km 139.7), 2695-066 Bobadela, Portugal

² GeoBioTec, Universidade de Aveiro, Aveiro 3810-193, Portugal

³ Departamento de Geociências, Universidade de Aveiro, Aveiro 3810-193, Portugal

especially to human beings, with the ingestion of those plant tissues (Kabata-Pendias 2001).

Several studies have been performed in order to assess the fate and behavior of the trace elements in the environment all over the world, namely the bioaccumulation of trace elements. These studies have been carried out in lichens and in diverse parts of plants, like tree barks, grown in different types of soils, including the volcanic soils (Baxter et al. 2012; Cruz et al. 2013; De Nicola et al. 2003; Freitas et al. 2006; Godinho et al. 2008; Pacheco et al. 2001, 2002; Pacheco and Freitas 2009; Prudêncio 2007; Shagal et al. 2012; Wilson et al. 2009). Numerous works have shown that tree bark is an efficient biomarker to evaluate past organic (Clarkson et al. 2002; Hermanson and Hites 1990; Hermanson and Johnson 2007; Wen et al. 2009) and inorganic contamination (Lahd Geagea et al. 2007, 2008a, b; Senhou et al. 2002), along with “natural enrichment” on metals and other trace elements in soils, and atmosphere. This is the case of soils from recent or even active volcanic regions, like Cape Verde archipelago, where some trace elements may occur in very high amounts that can have an impact on the health of plants and animals growing in (Marques et al. 2012, 2014a, b).

Due to the volcanic origin of the Cape Verde islands, there was never a land connection and the islands must have been colonized from other parts of the world. The natural vegetation of this archipelago has been destroyed by agriculture practices, wood cutting, overgrazing, and more recently by afforestation. Within the different types of vegetation, a forest of *Acacia albida* previously covered the dry parts of this environment. Nowadays, this species disappeared and was replaced by *Prosopis juliflora* (Frahm et al. 1996). Acacias grow and survive in dry environments and have an important function sustaining the ecological and hydrological stability of arid and semi-arid ecosystems (Ludwig et al. 1999).

In the present work, barks of acacia (*P. juliflora*) were collected in different geological formations of the Fogo Island (Cape Verde). The corresponding soils were also studied. Chemical analyses of bark and soils were performed by instrumental neutron activation analysis (INAA) allowing to obtain the concentration of Ba, Br, Co, Cr, Cs, Fe, K, Na, Zn, and rare earth elements (REE).

The main goals of this study are as follows: (i) the evaluation of the chemical elements uptake, and the establishment of the chemical patterns/enrichment factors of the tree bark grown in volcanic soils in the semi-arid conditions of Cape Verde, and (ii) the bark response to differences in soil composition, the geographic location, and climate conditions. Thus, this work is a first approach to evaluate chemical elements uptake, including metals that can be a threat to health, by using tree bark as biomarker in the active volcanic island of Fogo (Cape Verde).

Material and methods

Studied area

The Cape Verde archipelago is located in the Atlantic Ocean, some 500–800 km westwards of Africa coast, and comprises nine inhabited islands and several islets (with a total area of 4033 km²). Fogo is the fourth bigger island of Cape Verde (area of 476 km²) and is located in the south-western part of the archipelago (Fig. 1a). This island is an active stratovolcano rising 2829 m above sea level. The Fogo Island has a semi-arid climate with an average temperature of about 25 °C, which can reach the 0 °C in Chã das Caldeiras (December and January); the rain occurs between July and October and the precipitation is largely influenced by elevation and wind- and leeward conditions. The north-east part of the island is considered the humid region, with a precipitation higher than 600 mm/year, and the arid regions are located in the south-west, with a precipitation of 160 mm/year. The vegetation of this semi-arid island is restricted and occurs mostly in humid valleys or windward regions (Olehowski et al. 2008). The volcanic rocks of Fogo are included in three main stratigraphic units: (a) a carbonatite unit exposed in fluvial valleys near S. Filipe (the oldest rocks of the island), (b) a major volcanic sequence related to the sub-aerial shield-building of the volcano (nephelinites and associated lavas with layers of scoria or tuffs, previous to the caldera formation), and (c) a post caldera sequence including several pre-historic and historic eruptions (Madeira and Brum da Silveira 2005; Madeira et al. 2005; Torres et al. 1998). Deposits (de/Lahar) also occur associated with the post-caldera formation, with no precise age attributed. Soils are in general incipient, and paleosoils occur mainly in the western part of the island (Marques et al. 2014a).

Twelve acacia bark samples, as well as the soil underneath them, were collected in November 2010 in different country areas of Fogo Island (Cape Verde), corresponding to all the geological formations of the island: five samples in soils developed in the pre-caldera formation (carbonatite, nephelinites and associated lavas (herein referred as nephelinites), pyroclasts, and tuffs); and seven samples in soils from the post-caldera formation (lavas, pyroclasts, and deposits) (Fig. 1b, Table 1).

Sampling, treatment, and analysis

Thin layers of the acacia bark (not exceeding 0.5 cm) were carefully removed at an average height of 180 cm above the ground level, and away from the road. At the base of the trees, topsoil samples (0–20 cm depth) were also collected, using a

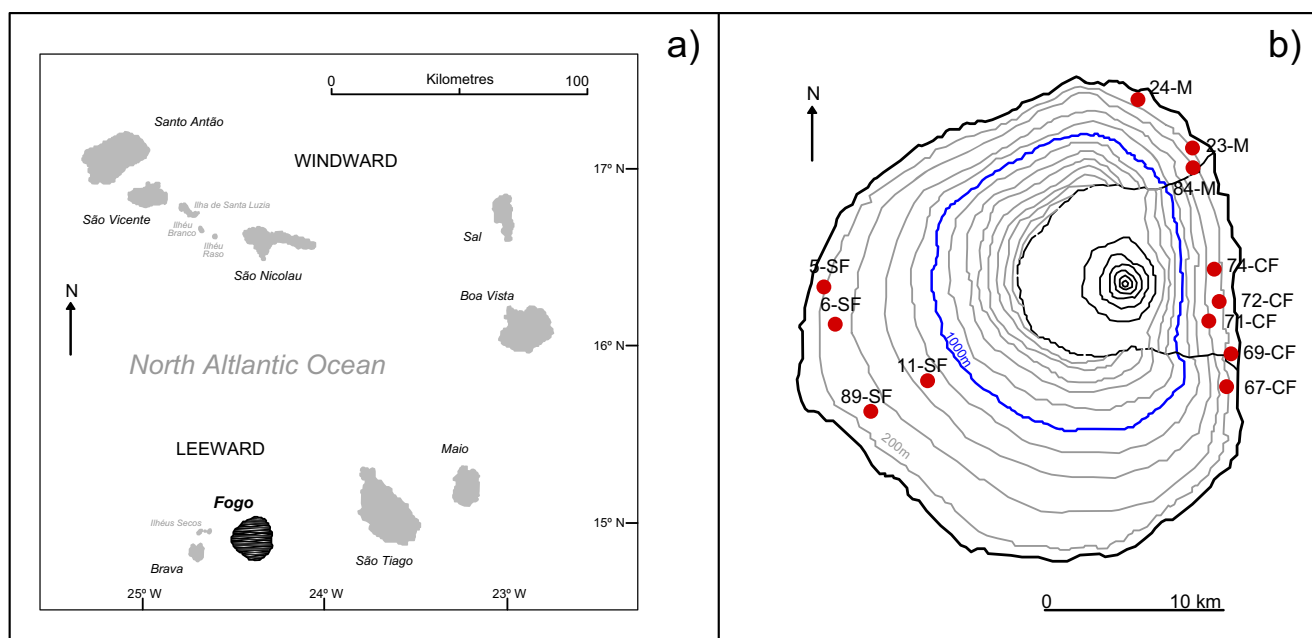


Fig. 1 a Location of Fogo Island (Cape Verde archipelago); b sample sites location of the 12 selected soils in Fogo Island, Cape Verde

stainless steel shovel to avoid contamination, and stored in polyethylene bags.

Prior to analysis, the bark trees were rinsed with deionized water during 30 s for the complete removal of dust and epiphytes, freeze-dried, and ground in Teflon™ mill. Pellets of ≈ 500 mg were done for k_0 -standardized INAA. Long (5 h) irradiations of the bark trees were performed in the Portuguese Research Reactor (RPI). Details of the irradiation conditions and measurements were described elsewhere (De Corte 1987, 2001; Freitas and Martinho 1989a, b; Freitas 1993; Pacheco et al. 2001). In the case of the soils, the whole sample was obtained by sieving through a 2-mm nylon mesh sieve, dried, and ground in agate mortars for chemical analysis. The total contents were obtained by comparative INAA method. Two reference materials were used, namely 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). Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). The samples and standards were prepared for analysis by weighing 200–300 mg of powder into cleaned high-density polyethylene vials. The irradiations (6 h) were also performed in the RPI (Dung et al. 2010). More details of the analytical method are given in Dias and Prudêncio (2007), Gouveia et al. (1992), Gouveia and Prudêncio (2000), and Prudêncio (2009). The precise and accurate concentration of 15 chemical elements was obtained (Ba, Br, Co, Cr, Fe, K, Na, Zn, and REE—La, Ce, Sm, Eu, Tb, Yb, and Lu).

Enrichment factors

In order to evaluate the enrichment of the chemical elements in plants with respect to the soil, enrichment factors (EF) were calculated, using Fe as conservative element according to:

$$EF_X = [X/Fe]_{\text{plant}}/[X/Fe]_{\text{soil}}$$

where EF_X stands for the enrichment factor of the element X in the tree bark, after having its concentration normalized to Fe concentrations in the corresponding soil sample. Iron was selected for normalization purpose due to its precise and accurate determination by INAA and its conservative behavior. In fact, the Fe^{3+} tends to remain in soils during the weathering processes in this type of soils/arid climate as shown by Marques et al. (2014b). Though unit or near unit EFs are usually considered unexceptional, the $EF > 10$ is accepted as a substantial enrichment over the natural background (Chiarenzelli et al. 2001; Galinha et al. 2010).

Results and discussion

The enrichment factors of the chemical elements in acacia barks and the chemical elements contents obtained by INAA in the underneath topsoils of Fogo Island are given in Tables 1 and 2, respectively.

In general, the results point to a significant bioaccumulation in bark of most of the chemical elements studied taking into consideration that $EF > 10$ is a reasonable enrichment factor by plants. Exceptions were found for Co, La, and Sm, which are not enriched in any of the acacia barks (Fig. 2).

Table 1 Acacia bark references (site number), enrichment factor of the studied chemical elements (normalized to iron), and geological formation/parent rock and chronology, for the studied samples of the Fogo Island (Cape Verde). The dates and parent rock of the post-caldera formation samples are according to Torres et al. (1998)

Enrichment factor (normalized to Fe)															
Bark reference	Ba	Br	Co	Cr	K	Na	Zn	La	Ce	Sm	Eu	Tb	Yb	Lu	Geol. form./parent rock
24	6.56	3380	0.834	16.0	1127	11.4	14.0	0.741	1.22	0.592	0.592	12.1	607	4439	Deposit (de/Lahar)
72	6.63	2521	0.712		519	4.56	33.7	0.365	1.44	1.30	0.891	12.1	18.3	3001	Deposit (de/Lahar)
69	27.7	170	0.964		142	1.90	33.9	0.227	0.317	0.212	0.312	12.1	129	2085	Lava
23	9.30	2369	3.29	23.6	179	50.3	91.7	0.250				31.3	64.8	817	Lava
71	58.0	450	5.12	49.6	234	5.39	86.7	0.836			1.14	18.3		4133	Lava
74	36.8	722	0.980	20.4	162	8.37	76.7	1.98	4.11	1.25	1.50	10.1	290	83.4	Lava
84		833	2.01	1.74	160	6.12	80.8		0.824	0.254		10.7			Lava
89		1042	0.396	11.7	765	33.5	47.7	0.042	19.7	0.192			90.2		Nephelinite
67	57.5	17.1	1.37	13.0	3246	45.1	41.1	1.52	7.45	1.37	1.05	7.96	156	1722	Nephelinite
11	22.0	393	0.591	1.85	1516	59.0	24.6	0.493	0.793		94.6				Nephelinite
5	5.06	95.8	0.803	0.685	751	58.9		0.793	0.666	0.376	1.04	7.59	131	958	Nephelinite
6	3.29	1318	1.14		93.6	27.8	2.30	1.24	1.17	1.13	0.709			364	Carbonatite
Min	3.29	17.1	0.396	0.685	93.6	1.90	2.30	0.042	0.317	0.192	0.312	7.59	18.3	83.4	
Max	58.0	3380	5.12	49.6	3246	59.0	91.7	1.98	19.7	1.37	94.6	31.3	607	4439	

Post-caldera formation
 Contemporaneous of the post-caldera episodes
 1857
 1785
 1769
 Before 1721
 1664?
 Pre-caldera formation

~5 Ma

Table 2 Chemical results obtained by INAA of the whole sample (<2 mm) of topsoils of Fogo Island (Cape Verde) (expressed in mg/kg, except Na₂O, K₂O, and Fe₂O₃ which are expressed in wt% oxide; Fe₂O₃ and Cr contents data on Marques et al. (2014b) for samples 6-SF, 11-SF, 55-CF, and 72-CF)

Soil reference	Ba	Br	Co	Cr	Fe ₂ O ₃	K ₂ O	Na ₂ O	Zn	La	Ce	Sm	Eu	Tb	Yb	Lu
24-M	634	8.71	46.9	156	13.2	1.15	2.44	151	55.3	119	11.8	3.50	1.31	2.54	0.287
72-CF	606	2.59	46.4	77.8	14.0	2.12	3.32	96.4	51.5	107	9.91	3.24	1.17	2.53	0.293
69-CF	642	4.13	40.2	49.1	13.1	2.22	4.35	126	63.7	128	11.4	3.67	1.29	2.95	0.318
23-M	737	2.04	45.3	118	13.8	2.06	4.20	143	53.8	120	11.3	3.52	1.17	2.59	0.352
71-CF	629	4.02	41.4	66.2	13.0	2.46	4.47	91.2	57.6	113	10.4	3.35	1.23	2.65	0.276
74-CF	560	4.90	39.4	146	12.1	1.90	3.51	121	55.2	115	11.0	2.97	1.05	2.23	0.295
84-M	525	2.89	44.6	119	13.1	1.74	3.98	94.3	54.4	105	9.51	3.12	1.10	2.46	0.284
89-SF	622	24.5	52.2	146	15.0	0.940	1.16	116	66.6	123	12.7	3.90	1.25	2.85	0.317
67-CF	370	146	47.8	253	14.2	0.891	0.952	95.1	58.3	99.5	11.6	3.40	1.23	2.70	0.310
11-SF	1050	176	55.3	197	17.0	0.408	0.306	178	155	267	24.6	7.37	2.29	5.49	0.603
5-SF	449	83.5	53.2	285	14.5	0.743	1.05	n.d.	54.8	121	12.0	3.58	1.42	2.95	0.326
6-SF	659	4.92	41.2	41.1	12.1	2.17	0.461	232	105	219	18.2	5.95	2.21	4.49	0.410
Min	370	2.04	39.4	41.1	12.1	0.408	0.306	91.2	51.5	99.5	9.51	2.97	1.05	2.23	0.276
Max	1050	176	55.3	285	17.0	2.46	4.47	232	155	267	24.6	7.37	2.29	5.49	0.603

n.d. not detected

K and Na

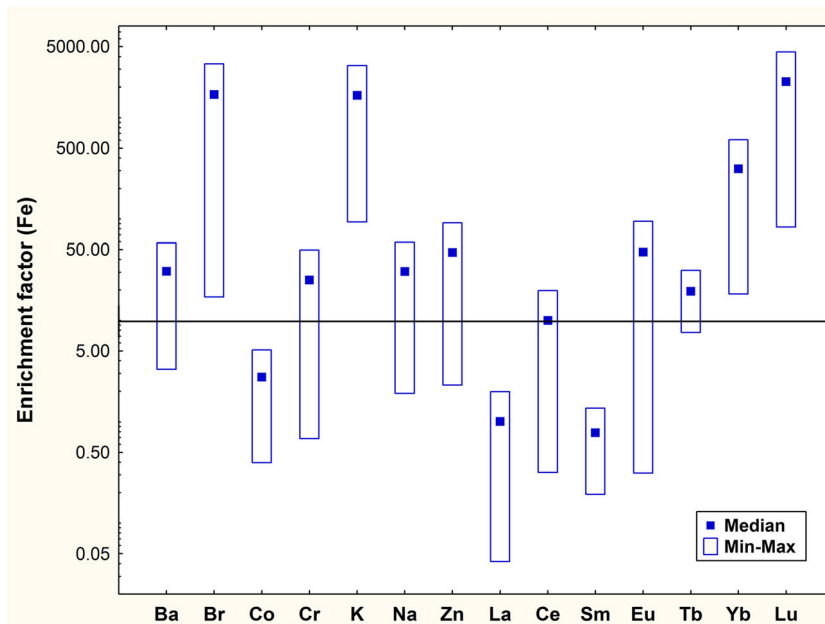
Potassium and Na, considered as essential or beneficial elements for the plant growth (Alloway 2009; ITRC 2001; Lucas 2001), occur in high amounts in the soils of the Fogo Island (Fig. 3a), particularly in those developed in the post-caldera formation. A high content of K in the soil developed on carbonatite was also found. Concerning bioaccumulation, all the acacia barks studied show high accumulation of K regardless of the geological context where the tree grows. This behavior could be expected since K participates in soil biological processes, plays an important role in water regulation, and has a rapid uptake in warm and aerated soils (Maurice 2009). Nevertheless, some variations in the EF_K are observed in acacia bark of the Fogo Island, with a tendency for higher enrichment factors in barks collected in the pre-caldera formation, particularly in the nephelinites (older soils), and in deposits (reaching an $EF_K=3246$) (Fig. 3b) despite the lower contents of K in these soils. This could be expected since K is available for plants uptake in volcanic soils probably due to its easy mobilization from the vitreous phase during weathering processes (Zharikova and Golodnaya 2009), and to the low amounts of minerals able to incorporate K namely alkali feldspars and secondary clay minerals. Besides, the EF_K found in the Fogo Island are very high when compared with tree barks grown in other volcanic environments namely in the Atlantic Pico Island (Azores, Portugal) (Pacheco and Freitas 2009), which can be partially explained by climate differences, particularly the lower precipitation in Cape Verde.

The acacia bark presents a curious behavior in the uptake of Na. Like K, a higher bioaccumulation in the soils from the pre-caldera formation ($EF_{Na}>10$) and a lower Na uptake in the soils from the post-caldera formation were found ($EF_{Na}<10$) (see Fig. 3b). This may be partially explained by the higher weathering degree of primary minerals like plagioclase and nepheline in the older soils with a consequent Na release and bioavailability. However, acacia barks collected on soils developed on lava of the post-caldera formation (23-M) and on deposits (24-M) from the north-east part of the island also show a high EF_{Na} , due to the rough topography and/or the higher precipitation in this part of the island, with a partial elution of this element after breakdown of primary minerals. The EF_{Na} in acacia bark of Fogo Island may reach high values when compared with the ones found in Pico Island, Azores (Pacheco and Freitas 2009).

Cr, Co, and Zn

Concerning the first transition elements (Cr, Co, and Zn), despite the high contents found in soils, the acacia barks present low contents, particularly of Co (Fig. 4a). In fact, there is no preferential uptake of Co by acacia in the different geological formations, being the $EF_{Co}<10$ for all the trees studied in this

Fig. 2 Minimum, maximum, and median values of the enrichment factor (EF, no units) of the chemical elements in acacia bark relative to soil in Fogo Island (Cape Verde), using Fe as conservative element



work (see Fig. 2). The results obtained indicate that in Fogo Island, the uptake of Zn by bark appears not to depend significantly on the parent rock/soil type. In fact, there is no significant difference in the EF_{Zn} of the tree barks grown in soils of the post-caldera (more recent soils) and pre-caldera (older soils) formations, with an $EF_{Zn} > 10$ for all the acacia bark studied, except for the one grown in carbonatites where the highest amount of Zn in soil was measured (Fig. 4b). Zinc is an essential nutrient and its soluble forms are the easiest to be uptake from soils by plants, being this process dependent of the plant type and the main soil conditions (composition and pH) (Alloway 2009). According to Loska et al. (2005), Zn is one of the most mobile elements in soil, and its content is affected by weathering of the parent material, precipitation, decomposition of living matter, and the use of soil fertilization. The deficiency on this element in the soil hinders plant growth, causes interveinal chlorosis and yellowing on young leaves, and reduces leaf size (Kabata-Pendias 2001). The high EF_{Zn} of tree barks found in Fogo, when compared with other Atlantic islands (Pacheco and Freitas 2009), can be explained by the higher content and availability of this element in this island. It should be noted that in a recent study performed by Marques et al. (2012) high contents of Zn and an aqua regia extraction of $\approx 50\%$ of this element were found in the volcanic topsoils of Santiago Island (Cape Verde). The occurrence of high contents of this element in soils of Fogo (68.8 to 232 mg/kg) is certainly from the natural background due to Zn compatibility during fractionation, through magmatic processes, and its enrichment in volcanic rocks. Also, the Zn adsorption in secondary Fe or Mn oxides has been suggested (Zampella and Adamo 2010), and the presence of Fe oxides including as nanoparticles was recently described by Marques

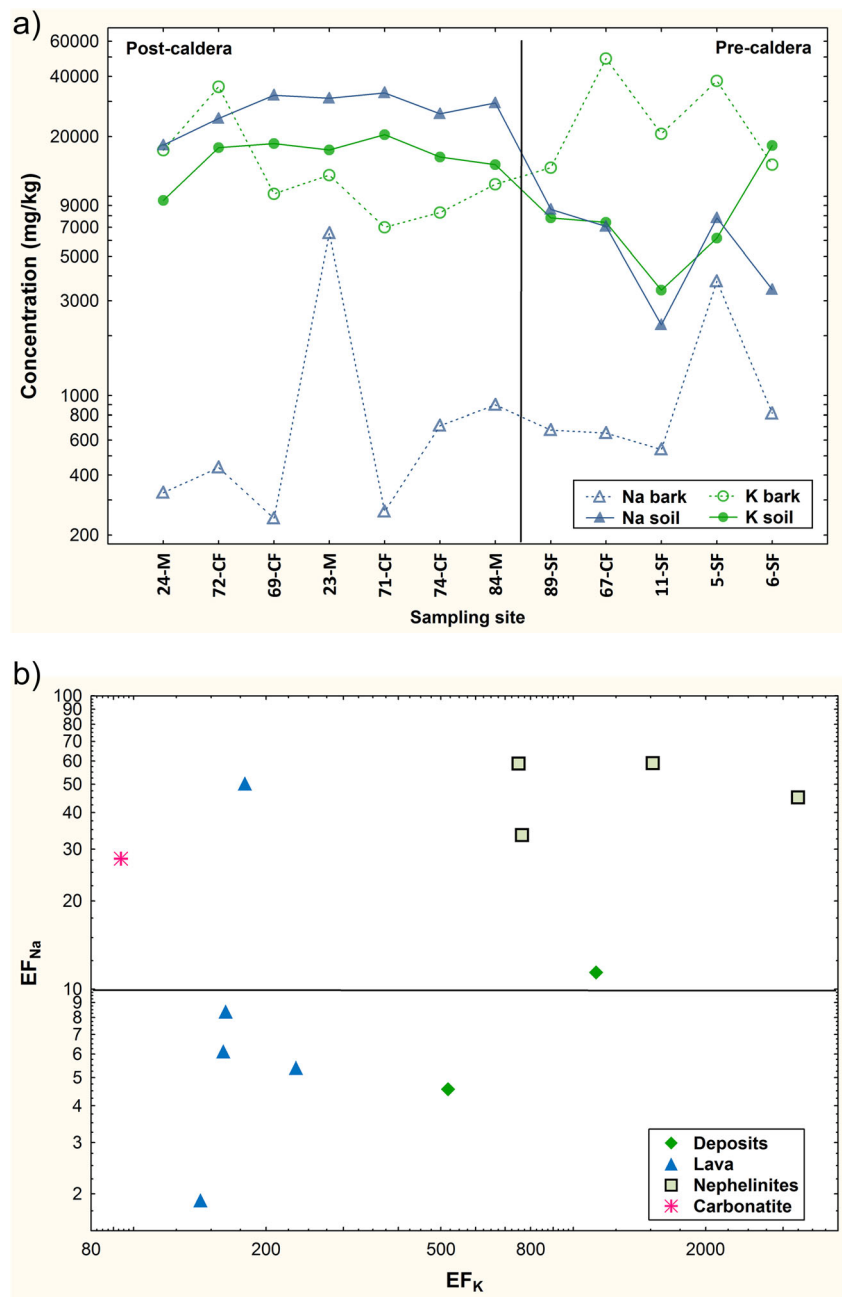
et al. (2014b) in this island. A considerable translocation of Zn from soils to leaves was observed in other volcanic soils by De Nicola et al. (2003) in Vesuvius National Park.

Chromium occurs in higher amounts in soils developed in the pre-caldera formation, with exception of carbonatite (see Table 2 and Fig. 4a). In a previous study of topsoils of Fogo Island (Marques et al. 2014b), this was already mentioned and explained based on the higher concentration of Fe oxide nanoparticles in the older soils, where Cr appears to be concentrated. Thus, despite the high EF_{Cr} found in most of the trees studied (see Table 1), the acacia barks from pre-caldera formation do not show the same trend, pointing the results to non-availability of the Cr portion incorporated in Fe oxides nanoparticles. In this way, Fe oxides appear to play an important role in the retention of Cr, which is considered of risk to environment (Marques et al. 2014b; Shanker et al. 2005).

Br and Ba

Bromine occurs in higher amounts in the older soils, except the one developed on carbonatite (Fig. 5), and is generally enriched in the acacia barks (all samples have $EF_{Br} > 10$) (see Table 1). The high EF_{Br} in tree bark grown in carbonatite soil may be partially due to the breakdown of fluorapatite and release of Br, where this element may be replacing F in the mineral structure (Marques et al. 2014b). Despite the low contents of Br in the younger soils of the post-caldera formation, this element is in general more accumulated in bark; this can be in part explained by the geographic position of the sampling sites—higher windward north and east areas, and more precipitation. In this part of the island, the parent rock/age factor appears to have no significance in soils as referred by

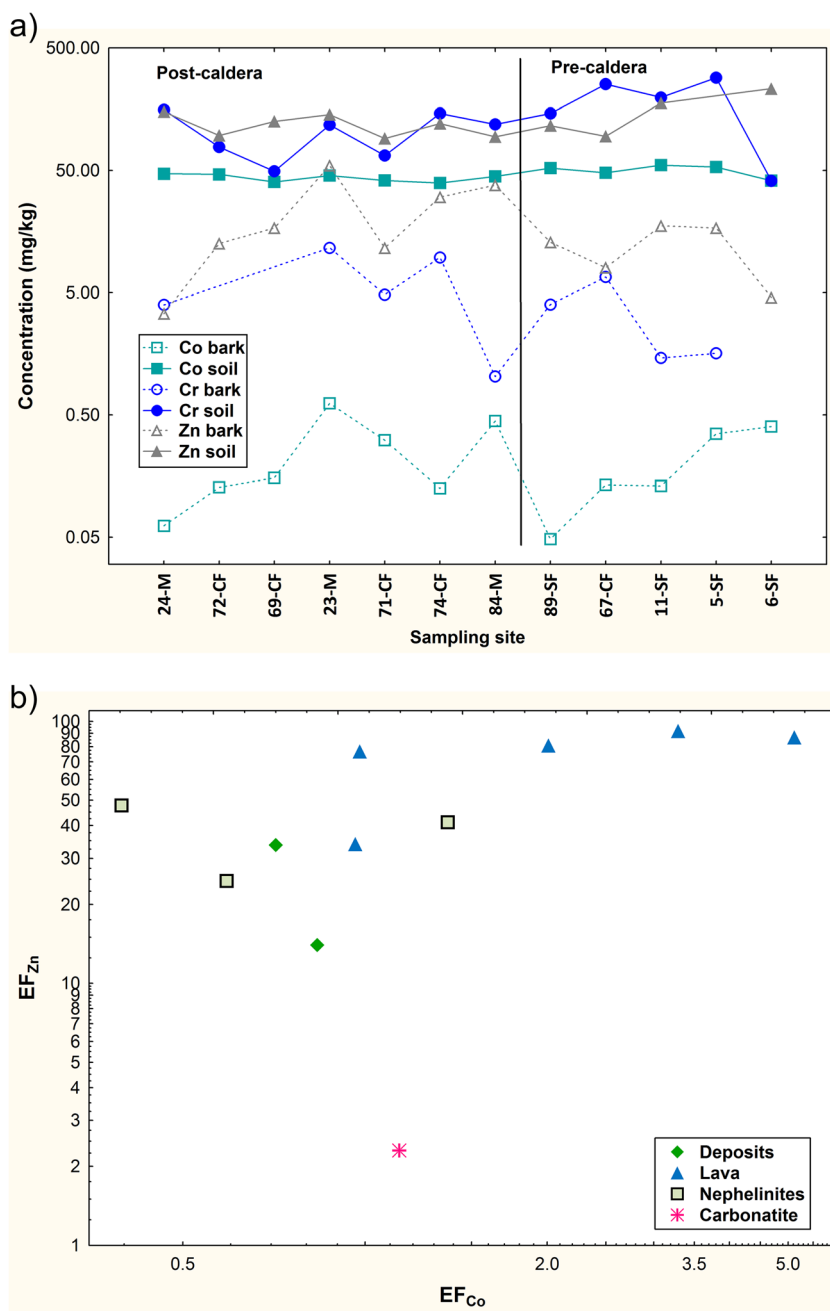
Fig. 3 **a** Total K and Na contents (mg/kg) in soils and in acacia barks for each sampling site in Fogo Island (Cape Verde); **b** enrichment factor of Na vs. enrichment factor of K in acacia barks



Olehowski et al. (2008). However, the glassy component of the soil may also contribute for a higher availability of Br; also volcanic ash soils tend to accumulate Br in its humic acid (Yamada 1968). Acacia barks from the eastern and northeastern part of the island present the highest Br accumulation ($EF_{Br} > 2000$), indicating that the contribution from the marine aerosol has to be taken in account since dominant winds blow from NE (60–80 %) (INMG 2010; Olehowski et al. 2008). In fact, tree barks collected in sites of high altitude and wind exposure have high EF_{Br} , which can be explained by the higher Br content in marine submicrometer aerosol (that can reach higher altitudes) and precipitation (Sander et al. 2003).

Barium was found in high amounts in the topsoils of Fogo Island (from 370 to 1050 mg/kg) and a high bioaccumulation of this element seems to occur ($EF_{Ba} > 10$) regardless of the geological context (Fig. 6 and Table 1) (Pearson correlation coefficient $\rho = 0.045$). Nevertheless, in the soils from the post-caldera formation, there is a tendency to higher Ba accumulation in the acacia bark. The different bioavailability of this element in soils may be due to its presence in different mineral phases, such as feldspars or barite. The occurrence of significant concentrations of Ba in volcanic soils of Cape Verde (Santiago Island) has already been mentioned by Marques et al. (2012). It should be noted that Ba is a toxic element to

Fig. 4 **a** Total Cr, Co, and Zn contents (mg/kg) in soils and in acacia barks for each sampling site in Fogo Island (Cape Verde); **b** enrichment factor of Zn vs. enrichment factor of Co in acacia barks



most plants, and its uptake may increase human and animals exposure through vegetable consumption (Monteiro et al. 2011).

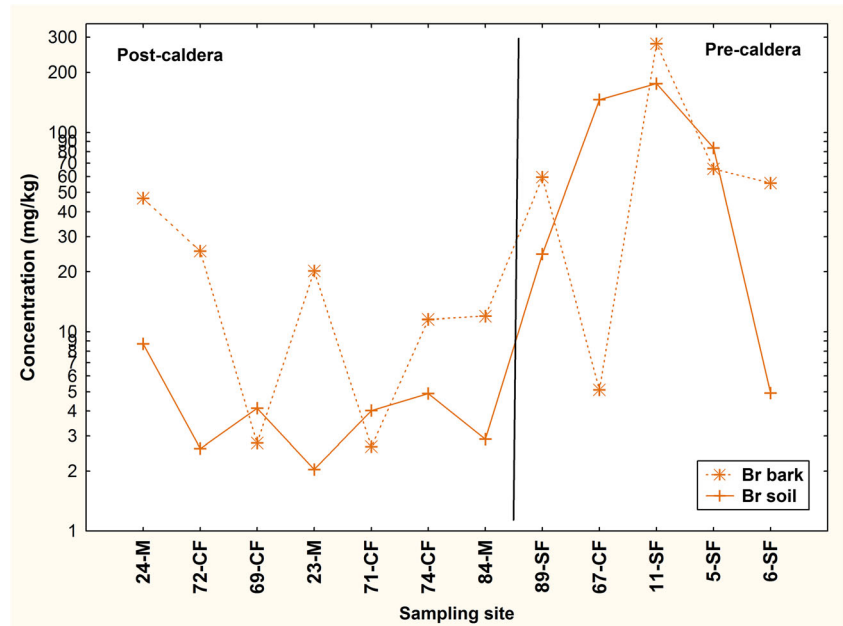
Rare earth elements

The REE patterns relative to chondrites (values of Anders and Grevesse (1989) multiplied by 1.36, obtained by Korotev (1996a, b)) of soils are shown in Fig. 7. The higher contents of REE are found in two soils from the pre-caldera formation: soil 11-SF (collected in nephelinites) and soil 6-SF (collected in carbonatites). The other studied soils show similar REE

patterns, with lower REE contents. A slight negative Ce anomaly occurs in soils 11-SF and 67-CF ($Ce/Ce^*=0.80$ and 0.79 , respectively).

The enrichment factor of REE vs. atomic number for acacia barks is shown in Fig. 8 (the acacia bark collected in site 11-SF was ignored since only a few REE contents in the bark were obtained). The REE patterns are in general similar for acacia grown in different geological formations with an increase from light REE (LREE)—those from La to Sm (i.e., lower atomic numbers and masses), to heavy REE (HREE)—those from Gd to Lu (higher atomic number and masses). A significant EF for the HREE was found, reaching $EF_{Lu}=4439$.

Fig. 5 Total Br contents (mg/kg) in soils and in acacia barks for each sampling site in Fogo Island (Cape Verde)



Concerning LREE and middle REE (MREE)—those from Pm to Ho, particularly from La to Eu, the acacia barks present in general low EF ($EF < 10$), with exception of Ce in acacia collected in nephelinite (site 89-SF) where a significant positive anomaly occurs (see Fig. 8).

The significant enrichment in HREE may be explained by the preferential uptake of these elements by bark after the pyroxenes breakdown, where smaller ions of the HREE substitute more readily than the LREE during magma processes. Also, HREE form soluble complexes more stable than the other REE partially explaining their presence in higher amounts in soil solutions (Henderson 1996). The LREE may

be partially incorporated in iron oxides and clay minerals, being less bioavailable (Compton et al. 2003; Prudêncio et al. 2011). Moreover, the positive Ce anomaly found in some of the acacia barks may be related with a partial Ce oxidation after the REE release from primary mineral phases and a favored uptake of Ce^{4+} by this type of plants. Previous studies have reported the uptake of cerium oxide nanoparticles ($nCeO_2$) by plants and their physiological impacts (Hernandez-Viezas et al. 2013; Lopez-Moreno et al. 2010a, b; Rico et al. 2013; Zhang et al. 2012). A similar trend for a higher retention of Ce relative to La in plants, compared to groundwater, was previously observed in the arid

Fig. 6 Total Ba contents (mg/kg) in soils and in acacia barks for each sampling site in Fogo Island (Cape Verde)

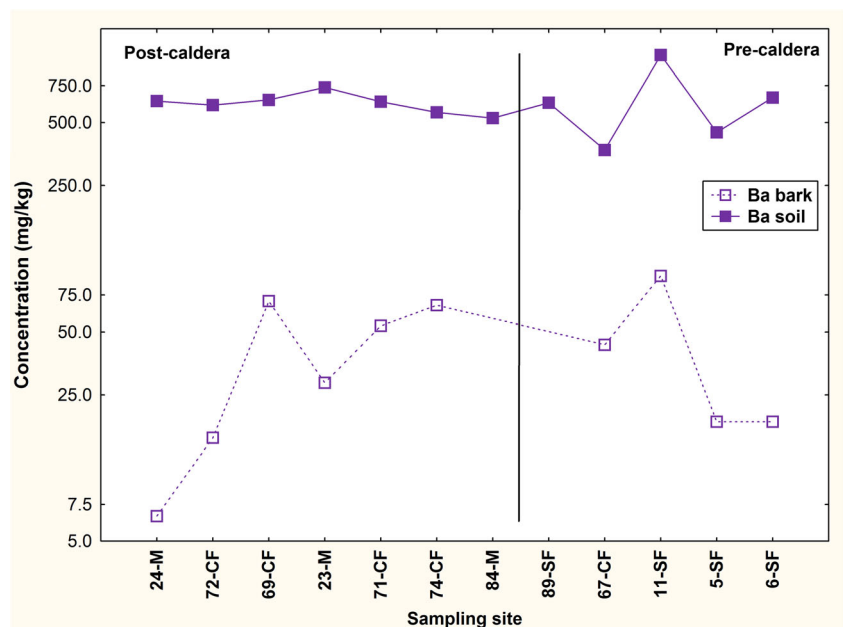
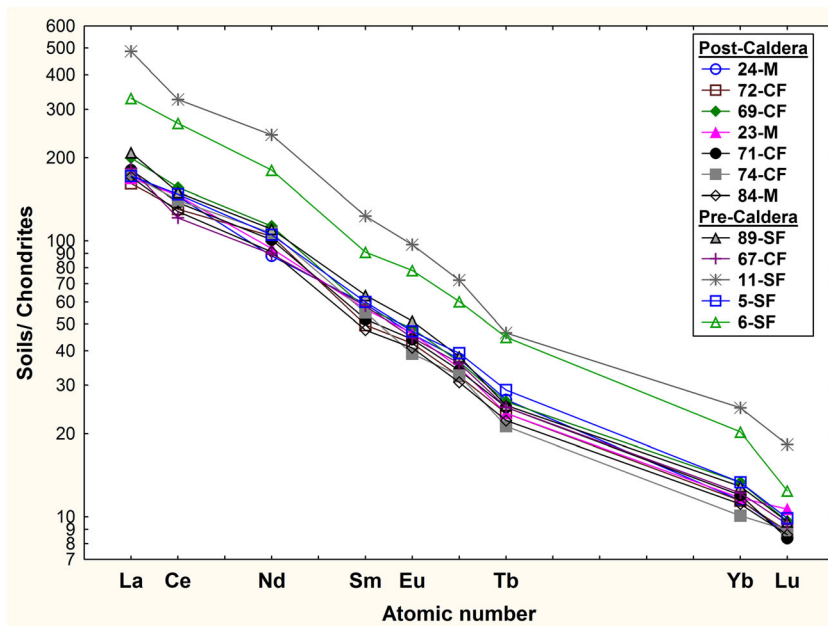


Fig. 7 Rare earth elements patterns (normalized to chondrites) of topsoils from Fogo Island (Cape Verde)



environment of AlKhod area, Oman (Sehmi et al. 2009), and in some tropical trees of Brazil (Nakanishi et al. 1997).

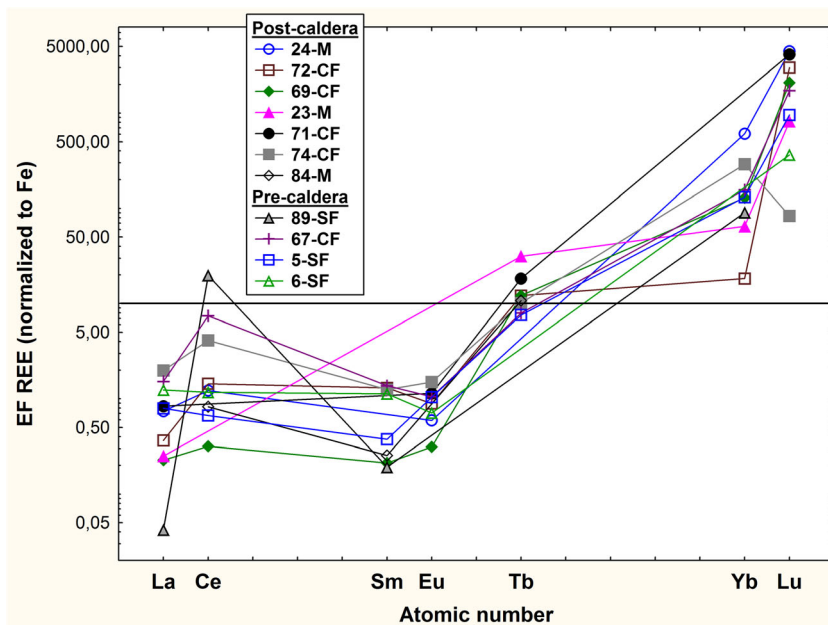
Despite the low solubility of the REE, their compounds are mobile under specific geochemical conditions, depending on pH, temperature, redox potential and the availability of potential ligands (Henderson 1996). The results obtained in this work show that REE may be significantly fractionated during biological processes in the volcanic soils of Fogo Island.

A previous work performed by Pacheco and Freitas (2009) in the Atlantic Pico volcanic island (Azores, Portugal) showed that, in general, the EFs of the chemical elements studied are

lower than the ones found in Fogo Island of Cape Verde. This can be explained mainly by differences in the climate, particularly the higher precipitation in Azores compared to the semi-arid environment of Cape Verde archipelago. Despite the high EFs in Fogo tree barks, the origin of the chemical elements (some that can be a threat to health) is certainly from the natural background rather than anthropogenic inputs since industry and the use of fertilizers is scarce.

Thus, the chemical elements may be significantly accumulated by plants grown in volcanic soils of Fogo Island, which can be explained mainly by the soil composition together with

Fig. 8 Enrichment factors of REE in acacia tree barks vs atomic number from Fogo Island (Cape Verde)



the semi-arid climate and a consequent bioavailability of chemical elements when rain drops fall in this environment with unimportant anthropogenic contamination input.

The results obtained in this work indicate that acacia bark can be used as effective biomonitor reflecting cumulative effects in environmental control, detecting anomalous concentrations of metal(oids) both from soil and atmosphere.

Conclusions

The acacia barks grown in diverse volcanic soils in the semi-arid environment of the Fogo Island (Cape Verde archipelago, Atlantic ocean) present high enrichment factors of the majority of the chemical elements studied (essential or not to plants), regardless of the geological formation where they grow. A significant bioaccumulation of essential elements to the plant growth, particularly K and Zn, occur as could be expected. A high uptake of Br was also observed for the majority of the trees, partially explained by marine/atmospheric contribution. In a lower scale, Ba and Cr also show a high bioavailability in the different types of soils where plants were collected. The HREE are preferentially uptake by tree barks relative to the other REE. A positive Ce anomaly was found in some tree barks indicating the uptake of nanoparticles of CeO₂ which can be expected since oxidation is the main chemical weathering process in the semi-arid climate of Fogo Island.

The high availability of chemical elements in the volcanic soils of Fogo Island is certainly due to long periods with no precipitation, leading to their accumulation and uptake by plants when water interferes. This bioaccumulation is surely from the natural background since no significant anthropogenic inputs occur in the island. Among the mineral phases present in soils, iron oxides nanoparticles can play an important role in the retention of potentially harmful elements like Cr.

As long-lived organisms, acacia barks of Fogo Island can be used as biomonitors to detect concentration of trace elements both from soils and/or atmospheric origin, and the results obtained in this work can be used as a benchmark if anthropogenic activities increase in the future to evaluate eventual pollution.

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