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Geochemical fingerprints in topsoils of the volcanic Brava Island, Cape Verde

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ABSTRACT

Topsoils developed on different lithologies of all the geological units of the volcanic Brava Island (Cape Verde archipelago) were studied by neutron activation analysis and Mössbauer spectroscopy. Sampling was performed according to the recommendations of the IGCP 259 ("International Geochemical Mapping"). Significant chemical contents variations were found even within the same volcano-stratigraphic unit, inherited from the parent rock composition under the semi-arid climate of the island. The chemical heterogeneity of topsoils within the same geological unit, particularly in the Upper Unit, was evidenced by a multivariate statistical analysis. Some differences found can be related with the geographical location/underlying basement. High contents of Mn, Co, Ga, Ba, La, Ce, Nd, Sm, Eu, Tb, Ta, W, Th and U were observed in soils related to carbonatites and phonolites. REE and W can be used to trace outcrops of extrusive carbonatites. In general iron is strongly oxidized occurring in the silicates structure as well as in hematite, oxidized magnetite and maghemite. The global iron oxidation degree, the fraction of Fe^{3+} in silicates and the fraction of nanosized oxides, which are higher in topsoils of the older units, may be an indicator of weathering degree. As, Br and Sb contents were also found to increase with weathering. Topsoils developed on extrusive carbonatites are clearly distinguished due to the absence of Fe^{2+} in the silicate phases and the remarkable predominance of low oxidized magnetite.

1. Introduction

The chemical elements content of soils and their spatial distribution constitutes a fundamental knowledge for many domains such as environmental monitoring, soil science, geology, mineral explorations, geomedicine (Inácio et al., 2008; Ódor et al., 1997; Prohic et al., 1997; Prudêncio et al., 2010, 2011; Rivera et al., 2015; Xuejing and Hangxin, 2001; Yang et al., 2010; Zhizhong et al., 2014). The analysis of whole samples to evaluate total concentrations determines the true extent of chemical elements levels in soils (Wilson et al., 1997). These data allow the assessment of the extractable fraction of the chemical elements by aqua regia digestion (Marques et al., 2012), by other acidic solution or by water (Sonneveld et al., 1990), thus contributing to a better understanding of the elements dynamics on the Earth surface. The use of topsoil or regolith samples for geochemical mapping is recommended by Darnley et al. (1995).

The geology, volcanology, geoecology and hydrogeology of the Cape Verde archipelago have been the subject of several studies (Assunção et al., 1965; Carreira et al., 2010; Gomes and Pina, 2003; Madeira et al., 2008, 2010; Matos Alves et al., 1979; Marques et al., 2014a, b, 2015; Martins et al., 2010; Monteiro Santos et al., 2006; Mourão et al., 2010; Pina et al., 2005). The first low sampling-density survey of the geochemistry of rocks, soils, stream and sediments was done in Santiago Island in the frame of a large project aiming to construct an environmental atlas of the Cape Verde archipelago. Soil samples were collected in 2005/2006 in Santiago with a density of 0.28 samples per km^2. Studies of these samples were performed including the chemical (aqua regia extractable solution) and mineralogical characterization, as well as grain-size distribution (Cabral Pinto, 2010; Cabral Pinto et al., 2014; Hernandez, 2008). The total content of major, trace and rare earth elements (REE), and the evaluation of the extractable fraction of selected elements by aqua regia digestion and its correlation with the grain size, was extensively discussed by Marques et al. (2012).

A detailed Fe speciation study by Mössbauer spectroscopy of topsoils of Fogo, another island of the same archipelago, showed that oxidation is a major weathering mechanism under semi-arid climate, and a correlation between the fraction of nanosized iron oxides and some trace

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elements that can be a threat to the environmental health was found (Marques et al., 2014b). Thus a similar study was considered to be of great importance for other Cape Verde islands.

In this work the first chemical results of topsoils collected on Brava Island in 2011/2013 (Cape Verde archipelago) are now presented. It should be noted that this sampling was performed before the 2014–2015 eruption in Fogo Island. During this eruption a significant amount of wind-borne ashes arrived at Brava Island.

Thus the main objectives of this work are: (1) the chemical characterization (total contents) of the whole sample (ø < 2 mm) of 43 topsoils developed on all geological units and sediments from Brava; (2) the iron distribution in mineralogical phases of topsoils; (3) the assessment of the ratio $Fe^{3+}/(Fe^{2+} + Fe^{3+})$ within and between the different geological units; and (4) the establishment of the geochemical baselines, geochemical patterns and chemical tracers of topsoils developed on Brava Island.

2. Geological setting, climate and study area

The Cape Verde archipelago (15–17°N, 23–26°W) is composed of 10 islands and several islets. They are located 600 to 900 km west of the African coast, on the southwestern part of the Cape Verde Rise (Fig.1A). Generally moderate, the climate of Cape Verde islands is characterized by stable temperatures with extreme aridity. The islands are affected by the two-season nature of the intertropical convergence zone (ITCZ). Precipitation levels are unpredictable, depending on how the ITCZ progresses and how much tropical moisture it carries. Years may pass with little or no precipitation. In dry periods significant soil loss also occurs through deflation. Among Cape Verde islands, Brava is one of the islands with more frequent rainy periods. Nevertheless, the semi-arid climate associated with the topographic features leads to incipient soils (Madeira and Ricardo, 2013). Brava (64 km^2) is the westernmost island of the ENE–WSW trending leeward group of the Cape Verde archipelago (Fig. 1B). It is characterized by an irregular plateau between 300 and 976 m above sea level, which is bounded by steep coastal cliffs and cut by fluvial incision in a generally radial drainage pattern. The plateau presents some aligned hemi-spherical hills formed by phonolite lava domes, a number of closed depressions that correspond to recent (Middle Pleistocene to Holocene) phreato-magmatic craters, and several NNW–SSE to NW–SE trending fault scarps that define a wide graben structure in the southern part. Marine and fluvial erosion and mass wasting processes also contributed to the present morphology of the island (Madeira et al., 2008). Field observations revealed the presence of an older basement composed of a submarine volcanic sequence (nephelinitic/ankaramitic hyaloclastites and pillow lavas) and an intrusive complex (alkaline–carbonatite) that is unconformably covered by younger sub-aerial volcanic deposits (dominated by phonolitic magmatism); sediments include alluvial and mass wasting deposits. These sequences allowed the definition of major volcano-stratigraphic units – Lower Unit, Middle Unit, Upper Unit, and Sediments (Madeira et al., 2010). The petrology and geochemistry of intrusive and extrusive carbonatites in Brava Island have been discussed in papers by Kogarko (1993), Hoernle et al. (2002), Mourão et al. (2010) and Mata et al. (2010).

3. Materials and methods

Forty-three topsoils (0–20 cm) were collected in 2011 and 2013 on Brava distributed as follows: (i) Lower Unit – 4 samples; (ii) Middle Unit – 3 samples; (iii) Upper Unit – 28 samples; and (iv) Sediments – 8 samples. The higher number of samples collected in the Upper Unit reflects its larger geographical area covered. The sampling locations of topsoils are shown in Fig. 1B, and some examples of studied soils/locations are shown in Fig. 2. Sampling was done according to the recommendations of the IGCP 259 ("International Geochemical Mapping"), with a density of 0.67 samples per km^2. Sample preparation included: in situ and laboratory sieving through a 2 mm nylon mesh, drying and grinding using an agate mortar (Darnley et al., 1995).

Chemical analyses of the whole sample (ø < 2 mm) have been performed by instrumental neutron activation analysis (INAA). The concentration of 30 chemical elements (Na, K, Mn, Fe, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, W, Th and U) was obtained. All powdered samples were prepared for irradiation by weighing 200–300 mg of powder into cleaned high-density polyethylene vials. Two multi-element reference materials were used, namely soil GSS-4 and sediment GSD-9 from the Institute of Geophysical and Geochemical Prospecting (IGGE). Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). The reference values were taken from tabulated data (Govindaraju, 1994). Short (90 s) and long (6 h) irradiations were carried out in the core grid of the Portuguese Research Reactor (RPI, CTN/IST) at a thermal flux of 3.96×10^{12} n cm^{-2} s^{-1}; $\phi_{thi}/\phi_{epi} = 96.8$; $\phi_{th}/\phi_{fast} = 29.8$. More details of this analytical method were published elsewhere (Fernandes et al., 2010; Gouveia et al., 1992; Sanjurjo-Sánchez et al., 2010).

The ^{57}Fe Mössbauer measurements were recorded in the temperature range 295 K–4.2 K in transmission mode using a conventional constant acceleration spectrometer and a 25-mCi ^{57}Co source in Rh matrix. The velocity scale was calibrated using an α-Fe foil at room temperature. Isomer shift values, IS, are given relative to this standard. Powdered samples were gently packed together with lucite powder into perspex holders, in order to obtain homogeneous and isotropic Mössbauer absorbers containing about 5 mg/cm^2 of natural iron. Low temperature measurements were performed using a bath cryostat with the sample in He exchange gas or immersed in liquid He at 4.2 K. The spectra were fitted to Lorentzian lines using a non-linear least-squares method (Waerenborgh et al., 1990).

Statistic data analyses (mean, standard deviation, minimum and maximum contents, and median) were performed. The chemical variability evaluation of the Brava topsoils, considering the different geological units on which they developed was done as follows: (i) the median values of Brava soils were compared with the median values of soils worldwide estimated by Bowen (1979) and the median values of topsoils developed on the different geological units of Santiago Island obtained previously by using the same analytical procedure (Marques et al., 2012); and (ii) the chemical composition of soils from each geological unit were compared with the median values of all the studied soils of Brava Island. Analytical errors and natural processes may shift the median ratios, therefore in this work the ratios >2 and <0.5 are assumed as significant enrichment and depletion, respectively.

In addition, multi-variate statistical clustering methods were employed by using the Statistica program (Statsoft, Inc., 2013), namely the joining tree-clustering (hierarchical) method, using the absolute concentration of the chemical elements as variables. The amalgamation rule employed in the joining tree-clustering was the unweighted pair group average, also referred as unweighted pair-group method using arithmetic averages (UPGMA). The Pearson correlation coefficient to evaluate correlations between variables was used. The k-means clustering procedure (non-hierarchical) was employed to classify cases into a specified number of clusters (k), comparing the within cluster variability to the between cluster variability of each variable (chemical contents).

4. Results and discussion

4.1. Geochemistry of elements

The total contents of chemical elements obtained in this work by INAA for the 43 Brava topsoils are given in Table 1. The sample reference, UTM coordinates, altitude, and geological unit/parent rock (following Madeira et al., 2010) for each soil are also given. The mean values and corresponding variation coefficient (%), median, and

minimum and maximum values of the chemical contents are given in Table 2. Significant variations occur in Brava topsoils - in general higher than 30%, reaching values higher than 80% for Br, Ba, La, and Ce.

The median values of the Brava topsoils as well as the median values of topsoils of Santiago Island (Marques et al., 2012), relative to the median values of Bowen (1979) (Table 2), are represented in Fig. 3A. In general, the studied elements are present in high amounts and significantly enriched (ratio > 2) in Brava, particularly Na, Mn, Co, Ba, La, Ce, Nd, Sm, Eu, Tb and Ta, and depleted (ratio <0.5) in As and Sb when compared to Bowen values. The median values of the chemical elements studied in both islands are higher in Brava, except for Sc, Br and particularly Cr, which is strongly enriched in Santiago Island; the higher contents of Ba, REE and other elements in Brava may be explained by the important occurrences of carbonatites (both intrusive and extrusive) and phonolites in this island, as already found by Kogarko et al. (2009) in calcite carbonatites of the Cape Verde archipelago.

The median values for the soils developed on the Upper Unit are similar to the median of all Brava topsoils as expected since this geological unit covers the largest area of the island and includes the majority of the studied samples (28 out of 43). The topsoils of the Upper Unit also present the highest chemical coefficient of variation: c > 30% (except for Fe, Ga and Ta), and c > 80% for Br, Ba, La, Ce and Nd. The main chemical variations observed for the other geological units are:

(1) Lower Unit – lower contents of K, Rb, Cs, Ba, La, Ce and Th; higher contents of Fe, Sc, Cr and Co particularly in topsoils developed on hyaloclastites where As and Br are strongly enriched, and Na depleted; the middle rare earth elements (MREE) are enriched relative to the heavy REE (HREE) and particularly to the light REE (LREE) (Fig. 3B).
(2) Middle Unit – lower contents of Sc, Cr, Co, Ga, Br, Sb, and higher contents of Na, Ba, REE, particularly the LREE, and W, which can be due to the influence of carbonatites - mixture of pyroxenites/ijolites with extrusive carbonatite in sample 25-BRV, and fenitization in the sample 27-BRV (Fig. 3C).
(3) Sediments – present a high variation in the chemical composition certainly related with variations in the composition of the respective source areas. Some topsoils developed on sediments can be distinguished: (i) sample 7-BRV which presents a chemical pattern with some similarities with the topsoils from the Lower Unit, particularly low LREE/MREE ratios and low K, Rb, Cs, and Th contents; (ii) samples 28-BRV and 29-BRV present a pattern similar to that of topsoils from the Middle Unit, with low Sc, Cr, As, Br, Sb, and high Ta, U, and REE (particularly the LREE) contents; and (iii) samples 2-BRV, 22-BRV and 32-BRV with high Ba contents and high LREE/MREE ratios. Topsoils with high LREE/MREE ratios tend to have higher Mn concentrations (Fig. 3D).

The results obtained show that the chemical contents of the studied elements may vary significantly within each geological unit, particularly in the Upper Unit which is certainly related to significant differences in the composition of the parent rock materials namely extrusive carbonatite ashes, phonolitic volcanic products (lava flows, domes and pyroclastic deposits), as well as mafic volcanism (see Table 1).

A multi-variate statistical approach (k-means method) applied to the topsoils of all geological units allows the establishment of chemical groups, clearly showing that the topsoil developed on carbonatite ashes was differentiated (Group 5 = sample 26-BRV), mainly due to higher contents of Mn, Zn, Ba, REE, W and Th (Fig. 4). The remaining samples were divided in four groups, and the allocation of the samples is indicated in Table 1 (chemical group):

Group 1 – includes the four topsoils from the Lower Unit, topsoils developed on phonolites (1 lava, 2 pyroclasts) and on mafic rocks (2 pyroclasts) of the Upper Unit, and two sediments; the variables with lower variance within the group are La, Ce, Nd, Eu, Mn, Zn, Yb, and Th. The mean values show that this group is mainly differentiated by higher contents of Fe, Sc, Cr and Co, and lower contents of Zn, Zr, Th and U.

Group 2 – includes one topsoil developed on pyroxenites/ijolites of the Middle Unit, topsoils developed on phonolites (6 lavas, 8 pyroclasts, and 2 pyroclasts with carbonatite influence) and one on mafic pyroclasts from the Upper Unit, and three sediments; the variables with lower variance within the group are all REE, Rb, and Th. The mean values pattern is the most flat comparing to the other groups.

Group 3 – includes two topsoils of the Middle Unit (one pyroxenite/ijolite with influence from extrusive carbonatites, and one pyroxenite/ijolite with evidence of fenitization), one developed on phonolite pyroclasts of the Upper Unit close to the Minhoto fault zone (see Fig. 1), and three sediments; the variables with lower variance within the group are Br, Co, Lu, Yb, Dy, and W. The mean values show that this group is mainly differentiated by high contents of Na, Mn, Zn, Rb, REE, W, Th, U, and particularly by the higher value of Ta.

Group 4 – includes four topsoils developed on phonolite pyroclasts from the Upper Unit, collected in the central-eastern area of the island; this group presents the highest chemical homogeneity, and the variables with lower variance within the group (in increasing order) are Ba, Sb, Ga, Ce, Th, Sc, Eu, La, Ta, Co, Tb, Nd, W, Cr, Sm, Yb, and Dy. The mean values show that this group is clearly differentiated by high contents of K, Ga, As, Rb, Zr, Sb, Cs, Hf and Th.

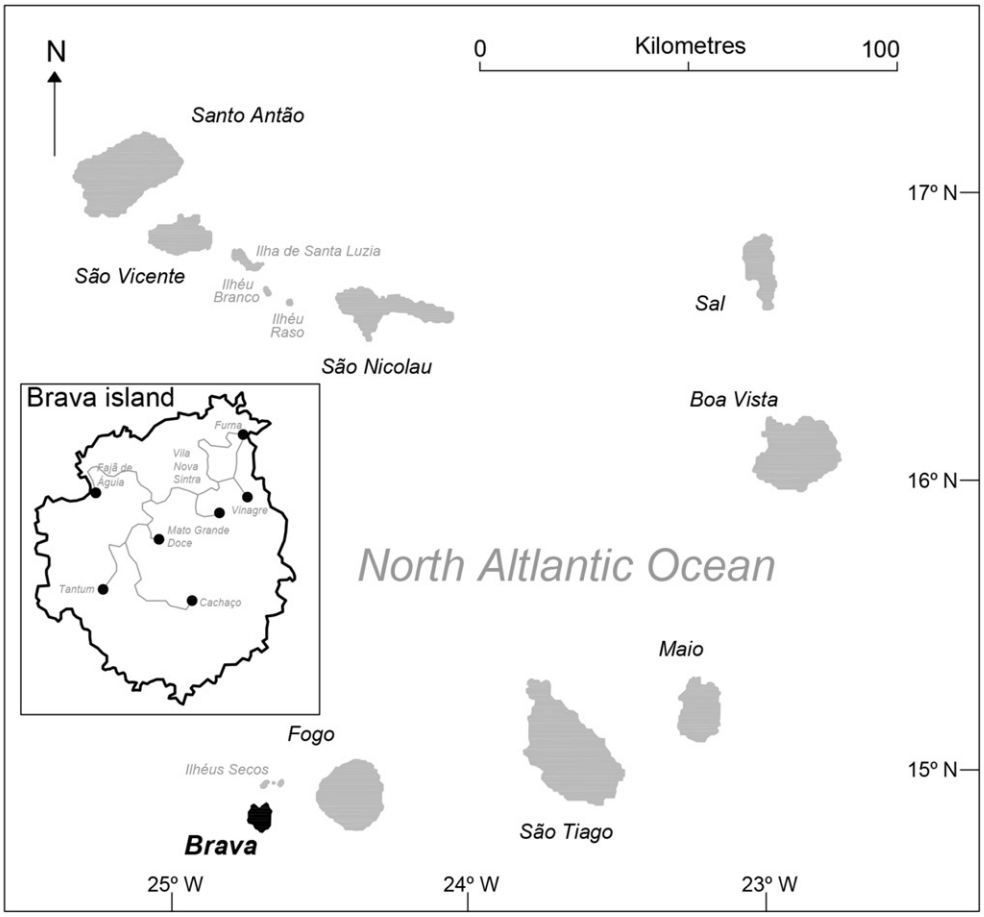
As expected the chemical groups formed do not distinguish topsoils per geological unit, or even per lithology. Nevertheless, this statistical approach contributed to: (i) identify zones within the same lithology with significantly different geochemical patterns (Group 4); and (ii) relate sediments rich in chemical elements like REE and U with provenance materials that include carbonatites and pyroxenites/ijolites with evidence of fenitization (Group 3).

The clear distinction of topsoils developed on extrusive carbonatites, mainly due to high concentrations of REE and W, allowed the identification of outcrops of extrusive carbonatites (sample 5-BRV) or with influence of these materials (sample 43-BRV), which were not identified by Mourão et al. (2010).

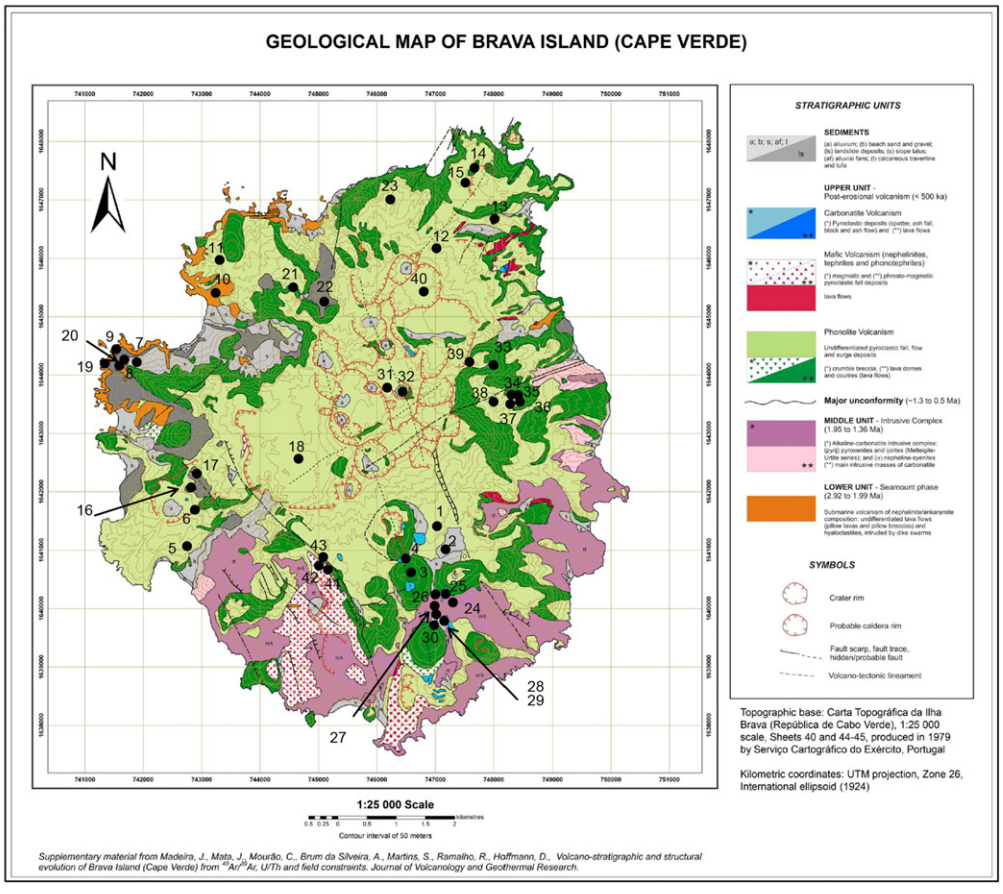
The chemical heterogeneity of topsoils within the same geological formation, particularly in the phonolitic pyroclasts of the Upper Unit, evidenced by the statistical analysis, was found to be related with the geographical location/underlying basement (the Lower Unit in northern Brava and the Middle Unit in the south). In fact topsoils developed on pyroclasts from the central eastern part of the island (Group 4), south to the Minhoto fault, are richer in K_2O, Ga, As, Rb, Zr, Sb, Cs, Hf, Th and U than those developed on pyroclasts from phreatomagmatic craters of the northern part of the island (Group 2). This heterogeneity in topsoils mainly reflects differences in the chemical composition of the parent rock due to the assimilation of different types of materials during magma ascent.

Fig. 1. (A) Location of Brava Island in the Cape Verde archipelago and (B) sampling location of 43 studied topsoils of the Brava Island (superposed to the Brava geological map by Madeira et al. (2010)).

A



B



Supplementary material from Madeira, J., Mata, J., Mourão, C., Brum da Silveira, A., Martins, S., Ramalho, R., Hoffmann, D., Volcano-stratigraphic and structural evolution of Brava Island (Cape Verde) from $^{40}Ar/^{39}Ar$, U/Th and field constraints. Journal of Volcanology and Geothermal Research.

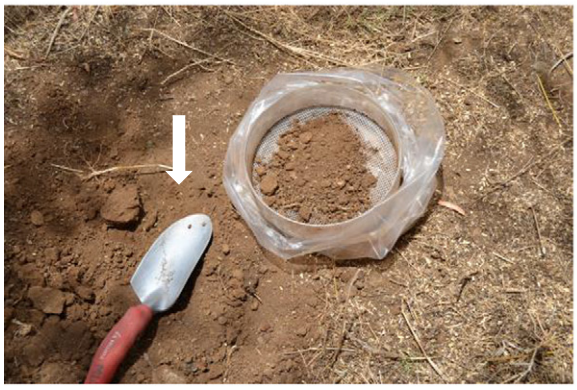
A

B

C

D

E



F

G

H

Table 1
Sample references, UTM coordinates (m), altitude (m), geological unit/parent rock, chemical group and chemical composition of the 43 topsoils of Brava Island (Cape Verde) (major elements in % w/w, and trace elements in mg/kg).

Field reference	1-BRV	2-BRV	3-BRV	4-BRV	5-BRV	6-BRV	7-BRV	8-BRV	9-BRV	10-BRV	11-BRV
X	747105	747158	746526	746473	742789	742684	741894	741631	741421	743210	743421
Y	1641368	1641053	1640631	1640842	1641105	1641736	1644210	1644210	1644421	1645421	1645842
Altitude	600	580	630	610	170	280	80	50	20	100	170
Geological unit	Upper	Sediments	Upper	Upper	Upper	Upper	Sediments	Sediments	Lower	Lower	Upper
Parent rock	Phonolite lava	Alluvium	Phonolite lava	Phonolite lava + Carbonatite	Phonolitic pyroclasts + extrusive carbonatite	Phonolitic pyroclasts	Slope talus	Landslide deposits	Hyaloclastites	Dyke swarm	Phonolitic pyroclasts
Chemical group	1	1	2	2	1	1	1	2	1	1	2
Na_2O	1.06	0.837	0.982	2.55	2.52	0.776	0.536	1.56	0.732	1.99	2.87
K_2O	2.59	2.14	3.36	3.69	1.73	1.12	1.19	3.13	0.71	2.10	2.53
Fe_2O_3T	14.3	14.8	12.2	5.45	10.4	14.2	16.4	11.5	19.6	8.04	8.50
Sc	18.3	16.3	16.9	3.45	16.6	27.0	30.3	17.1	37.9	32.1	13.1
Cr	161	82.2	162	34.1	73.1	270	148	108	126	323	138
Mn	2571	2610	2618	2060	2176	2037	1572	2331	2610	1046	1425
Co	39.4	36.0	38.1	7.02	31.6	56.3	59.5	37.1	80.3	69.8	24.7
Zn	198	154	157	179	125	110	153	212	120	138	121
Ga	28.4	37.0	33.7	34.1	26.1	28.5	25.3	33.3	34.8	30.5	44.0
As	1.54	3.49	4.80	1.51	4.46	0.994	2.05	3.49	3.92	2.38	2.61
Br	17.7	20.3	67.9	8.86	2.36	11.0	13.9	21.5	16.1	4.90	9.70
Rb	139	95.6	164	130	78.4	64.5	34.3	112	28.9	55.0	113
Zr	528	635	541	807	495	472	366	467	482	482	1121
Sb	0.224	0.227	0.315	0.127	0.271	0.257	0.274	0.230	0.320	0.300	0.274
Cs	2.20	2.21	3.31	3.42	1.59	1.38	0.725	2.20	0.655	0.584	2.76
Ba	1051	1642	897	5312	834	1176	286	865	490	663	447
La	99.3	135	96.6	125	149	88.6	51.0	71.0	85.4	74.4	59.2
Ce	194	290	171	240	265	150	89	145	126	142	114
Nd	77.0	125	76.2	110	122	80.3	56.6	61.0	98.9	82.2	59.4
Sm	12.9	17.6	11.2	11.2	20.3	11.8	11.2	10.5	20.1	14.1	9.90
Eu	3.89	5.56	3.21	3.82	6.13	3.69	3.42	3.08	6.06	4.38	2.98
Tb	1.25	2.19	1.51	1.26	2.29	1.4	1.36	1.36	2.19	1.70	1.36
Dy	7.84	8.98	7.28	7.01	11.3	6.77	6.81	6.35	12.1	8.04	6.89
Yb	3.46	5.26	3.67	4.08	4.60	3.02	2.60	3.18	4.52	3.74	3.77
Lu	0.358	0.622	0.444	0.500	0.527	0.374	0.346	0.421	0.597	0.395	0.453
Hf	10.9	13.2	11.2	16.0	8.11	10.0	7.31	9.87	8.65	9.56	22.4
Ta	6.46	7.8	5.22	5.03	6.31	4.39	4.24	5.30	4.94	6.53	9.28
W	0.874	2.44	1.91	1.27	7.12	1.22	1.56	2.18	1.87	2.71	2.53
Th	10.9	14.0	14.7	18.9	12.1	5.83	4.79	10.1	5.29	6.50	13.9
U	2.46	1.48	3.58	3.07	2.16	1.97	1.84	2.33	1.76	4.39	3.52

Fig. 2. Field photographs of topsoils sampling locations and/or details in Brava (Cape Verde). (A) Sample 9-BRV - Lower Unit, hyaloclastites; (B) Sample 24-BRV - Middle Unit, pyroxenites/ijolites; (C) Sample 33-BRV - Upper Unit, phonolite lava; (D) Sample 36-BRV - Upper Unit, phonolitic pyroclasts; (E) Sample 18-BRV - Upper Unit, phonolitic pyroclasts; (F) Sample 26-BRV - Upper Unit, extrusive carbonatite ash; (G) Sample 43-BRV - Upper Unit, mafic pyroclasts (close to carbonatite breccia); and (H) Samples 28-BRV and 29-BRV - Sediments, alluvium.

12-BRV	13-BRV	14-BRV	15-BRV	16-BRV	17-BRV	18-BRV	19-BRV	20-BRV	21-BRV	22-BRV
746947	748000	747631	747526	742842	742947	744631	741368	741684	744526	745053
1646158	1646579	1647526	1647210	1642053	1642368	1642579	1644210	1644263	1645473	1645158
450	110	220	210	350	400	650	30	50	500	520
Upper	Upper	Upper	Upper	Upper	Sediments	Upper	Lower	Lower	Upper	Sediments
Phonolitic pyroclasts	Phonolite lava	Phonolite lava	Phonolitic pyroclasts	Phonolitic pyr + Carbonatite	Landslide deposits	Phonolite pyroclasts	Hyaloclastites	Dyke swarm	Phonolite lava	Landslide deposits
2	2	2	2	2	2	3	1	1	2	3
5.23	1.14	1.09	1.33	2.37	3.19	1.78	1.2	2.52	2.45	3.22
3.52	2.54	3.00	2.51	2.54	2.17	4.60	1.39	1.22	2.76	2.18
7.77	10.0	9.21	9.96	6.75	8.73	12.5	18.6	12.6	9.36	13.6
9.53	13.7	11.8	11.1	7.38	12.8	7.85	26.5	13.2	14.8	23.7
93.1	134	93.9	89.3	41.9	110	68.2	238	76.4	111	131
1913	2076	1727	2052	1456	1882	5987	1727	1758	2060	4438
18.0	26.2	22.7	23.8	15.3	25.3	17.0	48.8	33.9	22.0	27.3
162	147	98.1	146	136	157	446	202	166	172	351
28.3	35.9	33.9	35.9	26.2	29.1	23.7	26.7	19.1	22.6	33.5
2.15	2.79	5.24	2.27	2.51	3.00	3.95	11.7	2.42	2.62	3.55
9.62	19.3	78.3	15.8	4.70	8.57	4.34	58.7	3.1	18.8	6.13
123	103	121	124	107	144	253	64.1	62.3	137	127
598	528	646	709	532	659	864	566	639	688	502
0.185	0.254	0.33	0.241	0.206	0.256	0.275	0.343	0.22	0.248	0.307
1.95	1.90	3.95	2.60	1.82	3.51	4.42	1.53	1.29	2.51	2.54
907	847	918	939	661	820	2916	525	721	911	1959
94.9	83.8	96.3	102	102	91.6	643	87.8	81.6	90.9	278
176	154	165	189	198	200	1108	152	184	184	464
73.1	67.3	63.5	86.2	80.5	82.2	355	66.7	91.2	77.5	188
10.8	11.4	11.3	13.6	11.1	8.32	32.9	13.0	11.4	9.45	24.7
3.5	3.39	3.41	4.18	3.69	3.74	11.1	4.77	5.15	3.88	8.33
1.29	1.35	1.38	1.64	1.2	1.14	3.32	2.03	1.88	1.67	2.37
6.84	8.05	8.01	7.55	7.36	6.3	14.2	9.00	8.45	9.44	11.0
3.76	3.69	4.02	4.13	3.72	3.76	7.68	3.84	4.24	4.42	6.83
0.482	0.469	0.547	0.496	0.416	0.472	0.897	0.467	0.436	0.582	0.843
11.4	11.5	12.2	13.0	9.20	11.0	13.3	10.1	11.5	12.3	6.92
4.98	5.73	4.68	6.79	4.32	5.12	5.74	6.95	7.96	5.33	3.89
2.99	1.68	3.21	1.90	2.69	4.34	4.1	2.35	3.56	3.10	4.27
13.8	11.3	14.2	13.2	11.7	12.5	29.8	10.1	8.99	14.8	21.1
2.32	2.81	2.63	2.24	3.21	2.32	7.16	2.13	2.21	1.34	3.80

(*continued on next page*)

Table 1
Sample references, UTM coordinates (m), altitude (m), geological unit/parent rock, chemical group and chemical composition of the 43 topsoils of Brava Island (Cape Verde) (major elements in % w/w, and trace elements in mg/kg).

Field reference	23-BRV	24-BRV	25-BRV	26-BRV	27-BRV	28-BRV	29-BRV	30-BRV	31-BRV	32-BRV	33-BRV
X	746210	747210	747105	746947	746894	746947	747053	746947	746158	746421	747947
Y	1647000	1640053	1640053	1640105	1639947	1639789	1639736	1639684	1643684	1643736	1644105
Altitude	260	510	490	480	460	430	430	440	790	780	540
Geological unit	Upper	Middle	Middle	Upper	Middle	Sediments	Sediments	Upper	Upper	Sediments	Upper
Parent rock	Phonolitic pyroclasts	Pyroxenites/ijolites	Pyroxenites/ijolites + extrusive carbonatite	Extrusive carbonatite - ash fall deposit	Pyroxenites/ijolites	Alluvium	Alluvium	Phonolite lava	Phonolitic pyroclasts	Alluvium	Phonolite lava
Chemical group	2	2	3	outlier	3	3	3	2	4	2	2
Na_2O	2.10	3.29	1.91	0.44	2.56	2.33	2.28	1.04	1.27	2.45	1.95
K_2O	2.40	3.56	2.27	0.507	2.15	3.17	2.69	2.79	3.73	3.94	3.53
Fe_2O_3T	10.8	6.1	10.6	9.23	9.68	12.8	11.8	11.2	9.68	9.54	8.35
Sc	17.3	1.01	2.70	1.45	1.54	5.06	5.20	15.8	10.6	10.3	9.68
Cr	106	6.28	27.0	21.0	13.9	62.1	50.6	102	87.4	80.9	70.0
Mn	1880	1634	3655	8054	2424	3299	3036	2238	3485	3005	1766
Co	26.7	8.10	18.5	5.61	13.0	19.8	18.9	31.2	21.4	19.7	18.1
Zn	195	148	380	312	128	257	231	173	303	252	184
Ga	22.5	25.5	21.1	27.6	26.2	52.0	46.1	37.4	52.2	40.2	48.8
As	2.47	2.73	1.93	1.96	2.86	1.57	1.21	3.32	5.28	2.59	5.94
Br	9.86	3.29	3.54	5.12	3.39	4.47	4.41	17.9	20.0	10.4	42.6
Rb	140	130	187	69.4	147	172	158	137	168	170	138
Zr	719	567	612	669	685	728	767	627	1348	741	609
Sb	0.264	0.102	0.0784	0.216	0.044	0.119	0.153	0.35	0.400	0.274	0.343
Cs	2.19	2.41	3.73	1.40	1.93	2.91	2.62	5.20	4.72	3.31	3.32
Ba	909	1656	1382	8274	1318	1098	1018	715	1087	1433	1100
La	114	106	390	813	209	267	235	114	143	163	93.7
Ce	250	227	699	1450	428	485	432	201	236	294	189
Nd	103	94.6	273	448	182	190	180	84.6	81.0	96.8	65.4
Sm	11.5	12.9	33.6	53.2	18.3	30.7	27.4	13.5	12.3	13.9	9.94
Eu	5.12	4.73	12.8	23.1	8.56	9.74	8.85	4.07	3.60	4.36	2.93
Tb	1.6	1.83	3.7	6.29	2.53	3.37	3.2	1.73	1.37	1.48	1.17
Dy	9.44	7.32	15.1	31.9	11.8	15.4	14.3	7.35	7.87	7.02	5.62
Yb	5.34	4.44	9.1	16.1	7.5	7.65	7.08	4.12	4.27	3.88	3.37
Lu	0.705	0.533	0.825	1.78	0.715	0.740	0.759	0.531	0.547	0.486	0.433
Hf	11.6	9.06	9.08	2.21	9.57	12.7	13.0	11.7	22.6	13.4	11.8
Ta	5.50	3.43	10.0	1.89	11.6	13.9	13.7	6.05	6.71	5.68	4.57
W	3.48	3.89	4.19	7.98	3.95	3.10	2.88	1.41	2.77	2.60	1.67
Th	15.9	13.6	15.1	34.7	11.8	13.4	12.9	13.5	26.2	16.9	17.5
U	1.90	4.61	2.48	3.04	2.26	7.33	7.35	4.55	5.57	4.10	2.63

34-BRV	35-BRV	36-BRV	37-BRV	38-BRV	39-BRV	40-BRV	41-BRV	42-BRV	43-BRV
748263	748368	748368	748263	748000	747631	746789	745316	745105	744947
1643789	1643684	1643421	1643474	1643474	1644210	1645421	1640368	1640526	1640789
400	400	450	470	480	550	475	650	660	670
Upper	Upper	Upper	Upper	Upper	Upper	Upper	Upper	Upper	Upper
Phonolitic pyroclasts	Phonolitic pyroclasts	Phonolitic pyroclasts	Phonolitic pyroclasts	Phonolitoc pyroclasts	Phonolitic pyroclasts	Phonolitic pyroclasts	Mafic pyroclasts	Mafic pyroclasts	Mafic pyroclasts
2	2	4	4	4	2	2	1	2	1
1.83	1.05	1.93	1.53	1.86	1.12	1.35	1.44	0.906	0.833
4.14	1.62	4.18	4.27	4.77	3.34	2.76	1.89	2.43	2.14
7.74	11.7	7.34	7.61	7.37	7.88	10.8	12.5	8.88	13.6
7.24	8.70	5.23	5.90	6.01	7.56	17.1	24.2	7.96	21.7
43.6	31.4	27.9	32.3	33.4	52.8	122	265	50.4	216
2370	2703	2362	2401	2323	2416	4221	1866	1835	2068
12.9	21.1	9.43	10.4	9.90	15.8	32.4	43.3	16.9	40.3
177	151	191	182	175	190	409	134	104	103
32.2	39.9	50.9	50.7	50.0	35.5	28.1	25.7	29.8	33.2
2.47	1.58	3.89	3.9	5.29	3.78	2.99	0.818	1.78	5.40
15.8	8.37	8.16	22.8	25.8	12.7	13.5	6.63	10.1	45.7
166	152	198	186	240	143	109	82.4	120	109
764	670	1087	1017	1109	738	431	367	633	612
0.264	0.182	0.407	0.417	0.416	0.299	0.406	0.138	0.151	0.116
2.92	2.28	5.06	4.57	6.73	3.00	2.73	1.15	1.97	2.19
1140	1054	1123	1233	1031	1262	1119	935	1530	2383
114	138	141	207	103	89.9	179	69.1	106	161
206	275	243	332	198	182	288	127	164	230
78.1	105	92.0	123	55.0	59.0	105	57.0	73.0	116
11.1	16.7	13.7	16.9	8.93	9.4	16.7	9.92	9.61	19.6
3.57	5.21	4.14	5.04	2.63	2.94	4.96	3.17	3.18	5.94
1.27	1.84	1.49	1.72	0.939	1.09	1.92	1.20	1.21	2.47
6.50	9.97	8.45	9.70	5.30	6.80	10.1	5.07	6.04	12.9
3.99	4.63	5.07	5.44	3.48	3.57	4.21	2.72	3.56	5.42
0.552	0.51	0.682	0.704	0.424	0.492	0.485	0.348	0.509	0.660
13.1	12.2	19.1	17.5	20.1	13.6	8.49	8.17	11.5	11.1
4.20	8.00	5.29	5.05	4.93	4.91	5.22	4.80	5.12	5.47
2.50	1.47	2.05	1.42	2.07	1.86	2.21	1.38	0.803	3.84
17.6	10.3	29.6	30.7	29.0	16.8	13.7	6.02	10.7	9.45
2.57	3.07	4.81	3.86	6.43	2.48	3.55	1.60	1.68	3.97

Table 2
Mean values and variation coefficients, median, minimum and maximum values of the chemical results obtained by INAA for 43 topsoils of Brava Island (Cape Verde), median values in soils estimated by Bowen (1979) and median values of 63 Santiago topsoils (from Marques et al., 2012) (major elements in % w/w, and trace elements in mg/kg).

	Brava Island (Cape Verde)					Soils (Bowen, 1979)	Santiago Island (Cape Verde)
	Mean	c (%)	Min	Max	Median	Median	Median
Na_2O	1.80	51.2	0.44	5.23	1.78	0.674	0.747
K_2O	2.67	37.9	0.507	4.77	2.54	1.69	1.38
Fe_2O_3T	10.69	28.9	5.45	19.6	10	5.72	14.3
Sc	13.34	64.7	1.01	37.9	11.8	7	24.9
Cr	100	71.9	6.28	323	87.4	70	590
Mn	2539	48.4	1046	8054	2238	1000	1803
Co	27.3	60.1	5.61	80.3	22.7	8	59.8
Zn	191	42.5	98.1	446	172	90	157
Ga	33.63	26.7	19.1	52.2	33.2	20	26.7
As	3.19	57.1	0.818	11.7	2.73	6	2.82
Br	16.7	102	2.36	78.3	10.4	10	15.6
Rb	128	37.4	28.9	253	130	150	54.1
Zr	670	30.6	366	1348	635	400	382
Sb	0.25	36.9	0.044	0.417	0.257	1	
Cs	2.68	48.0	0.584	6.73	2.51	4	1.7
Ba	1362	97.6	286	8274	1051	500	671
La	157	91.3	51.0	813	106	40	65.2
Ce	285	88.0	89.0	1450	200	50	143
Nd	113	69.3	55.0	448	84.6	35	64.3
Sm	15.8	54.2	8.32	53.2	12.9	4.5	11
Eu	5.35	66.4	2.63	23.1	4.14	1	3.38
Tb	1.87	50.3	0.939	6.29	1.60	0.7	1.29
Dy	9.29	47.0	5.07	31.9	8.01	5	6.76
Yb	4.81	46.8	2.60	16.1	4.12	3	3.1
Lu	0.57	40.4	0.346	1.78	0.509	0.4	0.38
Hf	11.9	32.6	2.21	22.6	11.5	6	8.53
Ta	6.12	39.4	1.89	13.9	5.30	2	6.27
W	2.73	52.5	0.803	7.98	2.50	1.5	
Th	14.97	47.1	4.79	34.7	13.6	9	8.18
U	3.27	47.7	1.34	7.35	2.63	2	1.64

4.2. Iron speciation

Mössbauer spectra (Figs. 5, 6 and 7) were fitted to sextets and doublets each corresponding to an Fe containing phase or to a set of unresolved contributions from Fe-bearing phases as explained in detail in Marques et al. (2014b). When sextets that identify iron oxides are only detected at 4 K (Fig. 5A), these oxides occur as nanoparticles (Coey, 1988; Murad, 1998; Vandenberghe et al., 2000). Results of the spectra analyses are summarized in Table S1 (supplementary material).

Topsoils developed in the Lower Unit (Fig. 5A) and in the Middle Unit (Fig. 5B) present some of the highest oxidation states, $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ for the whole sample, and for the silicate phases. Hematite and maghemite are the only iron oxides observed; practically all of them occur as nanoparticles. The Fe speciation strongly suggests that these samples are the most weathered in agreement with their longest exposure to weathering agents.

In the Upper Unit, topsoils developed on phonolite lava domes (Fig. 6A) or close to the extrusive carbonatite conduits where the phonolites were crossed by carbonatite magmas, are also strongly oxidized. The only Fe oxides detected in these soils are hematite and maghemite. Topsoils developed on phonolitic pyroclasts show the largest range of oxidation degrees, and the lowest fraction of iron oxides as nanoparticles. The topsoils developed on mafic pyroclasts have the lowest oxidation degree in Brava. The Mössbauer spectrum of 41-BRV taken at 295 K (Fig. 6B) shows in addition to Fe^{2+} and Fe^{3+} incorporated in silicate phases, oxidized magnetite and hematite. A large fraction of these oxides occur as bulk oxides since at room temperature it is already possible to observe their typical magnetic sextets.

The topsoil developed on carbonatite ashes (26-BRV) shows an iron oxidation degree $Fe^{3+}/(Fe^{2+}+Fe^{3+}) = 75\%$. No Fe^{2+} in silicate phases was detected. Approximately 79% of the total iron is present as little oxidized magnetite (Fig. 6C) confirming petrographic data reported by Mourão et al. (2010).

Sediments containing materials issued from phonolites, pyroxenites and extrusive carbonatites from the Middle Unit (28-BRV and 29-BRV) are similar and suggest mixing of the original materials. The only binary oxide observed in these sediments is hematite, partially as nanosized particles (Fig.7A). In the 8-BRV sediment sample (Fig.7B) with contributions essentially from phonolite lava and pyroclasts from the Upper Unit the oxidation degree is identical, within experimental error, to those of the above referred sediments. In addition to hematite, oxidized magnetite is also present.

It should be noted that the absence of goethite in all the studied topsoil samples is not common in continental surface soils but has already been reported in the case of weathering in semi-arid climates (Di Figlia et al., 2007; Marques et al., 2014a).

The significant variations found in Brava topsoils may be mainly inherited from the parent material in the semi-arid climate of Cape Verde archipelago, as already found for Santiago Island (Marques et al., 2012). The degree of iron oxidation is higher in topsoils of the submarine volcanic sequence (Lower Unit) and of the intrusive complex (Middle Unit), which compose the older basement of the Brava Island. Also a high proportion of nanosized iron oxides was found in topsoils of these units, particularly in those developed on submarine volcanic rocks, where the highest Fe, Sc, Cr, Co and As concentrations were found. A higher content of Cr and As was also found to be correlated with the concentration of nanosized iron oxides in Fogo Island (Marques et al., 2014b). The high U concentrations found in sediments (with contribution from the Middle Unit), may be explained by its incorporation in the nanoparticles of hematite, the only Fe oxide present (Marshall et al., 2014).

A positive correlation between $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ and the concentrations of As, Br, and Sb was found for most samples. In the case of Sb, the following exceptions occur: (i) topsoils from the Upper Unit developed on phonolitic pyroclasts in the central-eastern part of the island, present higher Sb contents than expected considering the iron oxidation degree (Group 4); and (ii) low Sb concentrations compared to the degree of iron oxidation were found in topsoils developed on pyroxenites, ijolites and carbonatites of the Middle Unit and on sediments with a significant contribution from these materials (Group 3).

5. Conclusions

The topsoils developed on Brava, collected before the 2014–2015 eruption in the neighboring Fogo Island, show significant chemical content variations for the majority of the elements studied, even within the same geological formation. These variations, particularly evident in the Upper Unit, were related with the geographical location, which reflects differences in the chemical composition of the parent rock/magma. High contents of lithogenic trace elements like Mn, Co, Ba, La, Ce, Nd, Sm, Eu, Tb, Ta, W, Th and U are found due to the occurrence of carbonatites and phonolites. REE and W are good indicators for extrusive carbonatite outcrops. In general iron is strongly oxidized. It occurs in the silicates structure, and as binary iron oxides, hematite, oxidized magnetite and maghemite. The global iron oxidation degree and the fraction of Fe^{3+} in silicates are higher in topsoils of the older units. The 26-BRV soil developed on extrusive carbonatites in addition to a lower iron oxidation degree is clearly

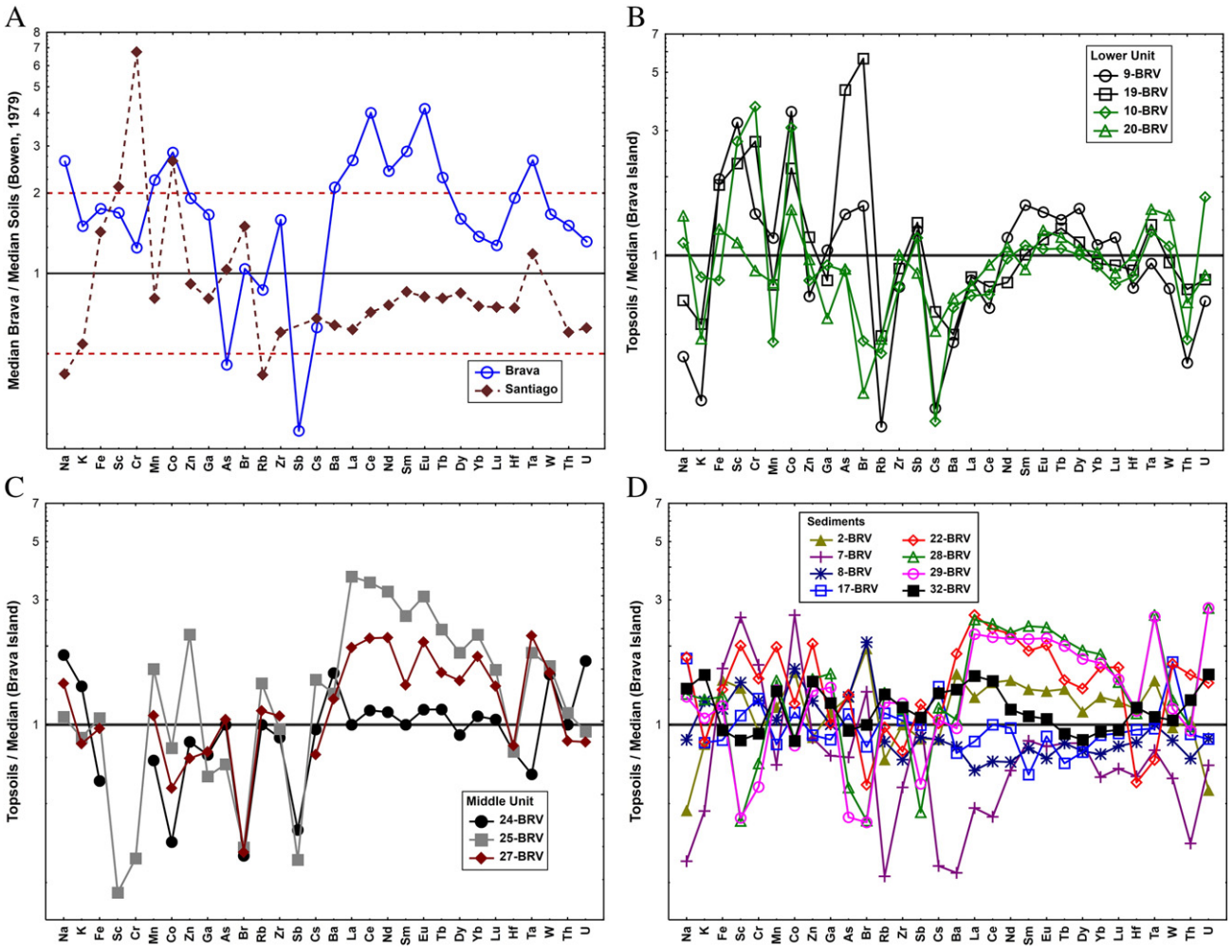


Fig. 3. (A) Median values of the chemical contents of topsoils from Brava, and from Santiago (data from Marques et al. (2012)) relative to the median values of worldwide soils estimated by Bowen (1979); and chemical contents in topsoils from the (B) Lower Unit, (C) Middle Unit, and (D) Sediments relative to the median values of all 43 topsoils studied in Brava.

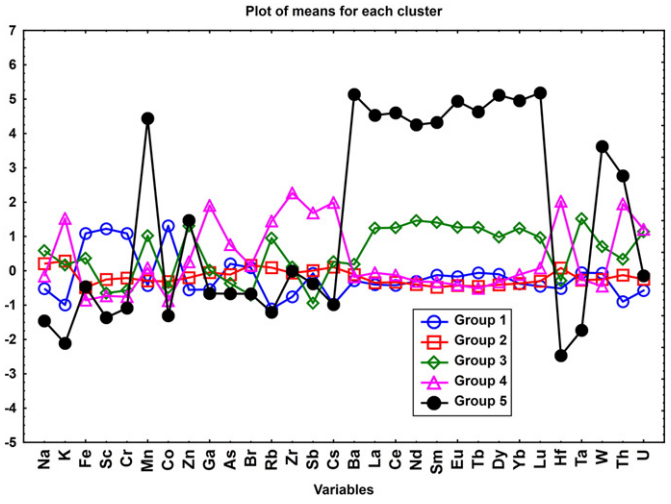


Fig. 4. Plot of means for each chemical group obtained by the k-means clustering method (k = 5), using as variables the total element concentrations in topsoils from Brava (Cape Verde).

different from the remaining ones due to the absence of Fe^{2+} in the silicate phases and the remarkable predominance of low oxidized magnetite.

Thus in general different chemical patterns of topsoils of Brava Island reflect the highly contrasting parent materials, and iron speciation is mostly correlated with weathering in the semi-arid environment in Cape Verde archipelago.

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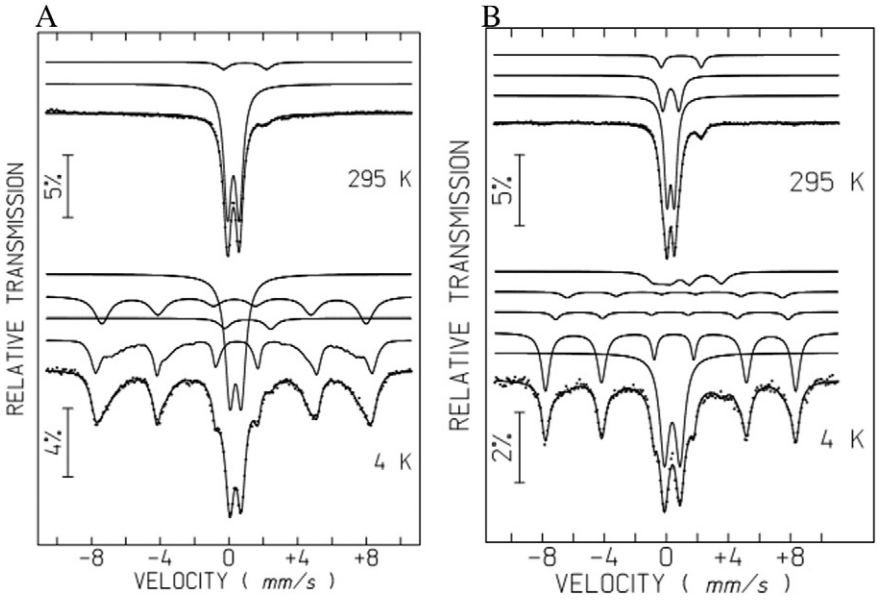

Fig. 5. Mössbauer spectra of (A) topsoil 9-BRV (Lower Unit, hyaloclastites) and (B) topsoil 25-BRV (Middle Unit, mixture of pyroxenites and extrusive carbonatite) from Brava (Cape Verde), taken at 295 and 4 K.

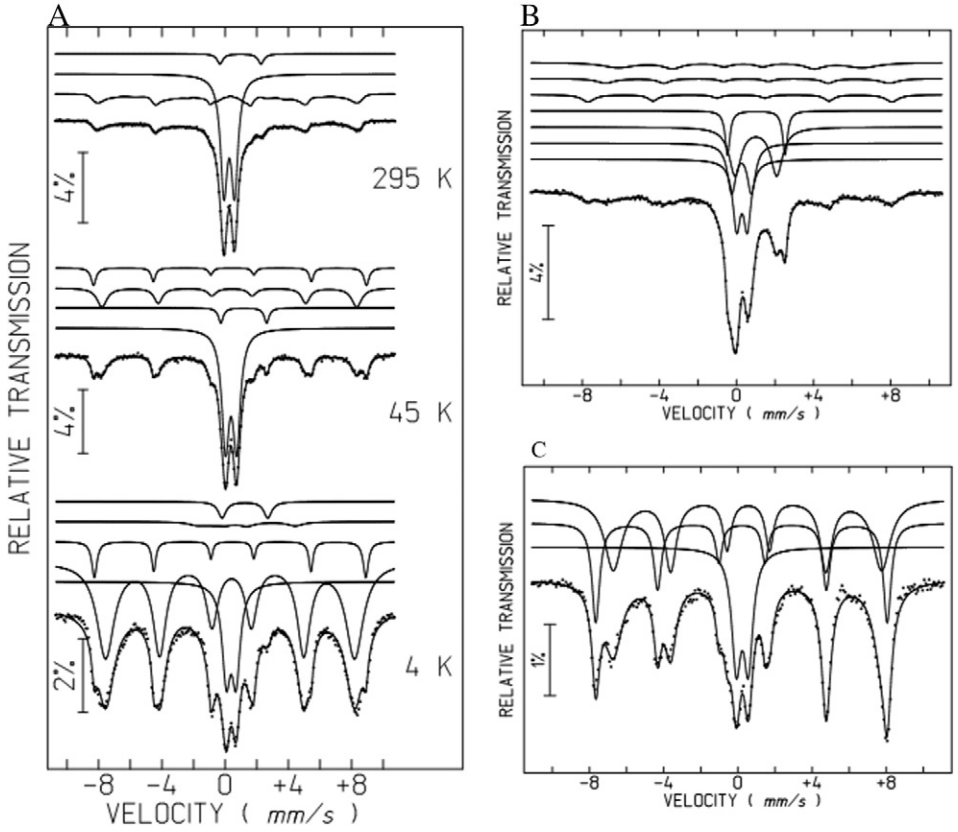

Fig. 6. Mössbauer spectra of: (A) 3-BRV topsoil (parent rock: phonolite) taken at 295 K, 45 K and 4 K; (B) 41-BRV topsoil (parent rock: mafic volcanism – phreato-magmatic pyroclastic fall deposits) taken at 295 K; and (C) 26-BRV topsoil (parent rock: extrusive carbonatite ashes) from Brava (Cape Verde), taken at 295 K.

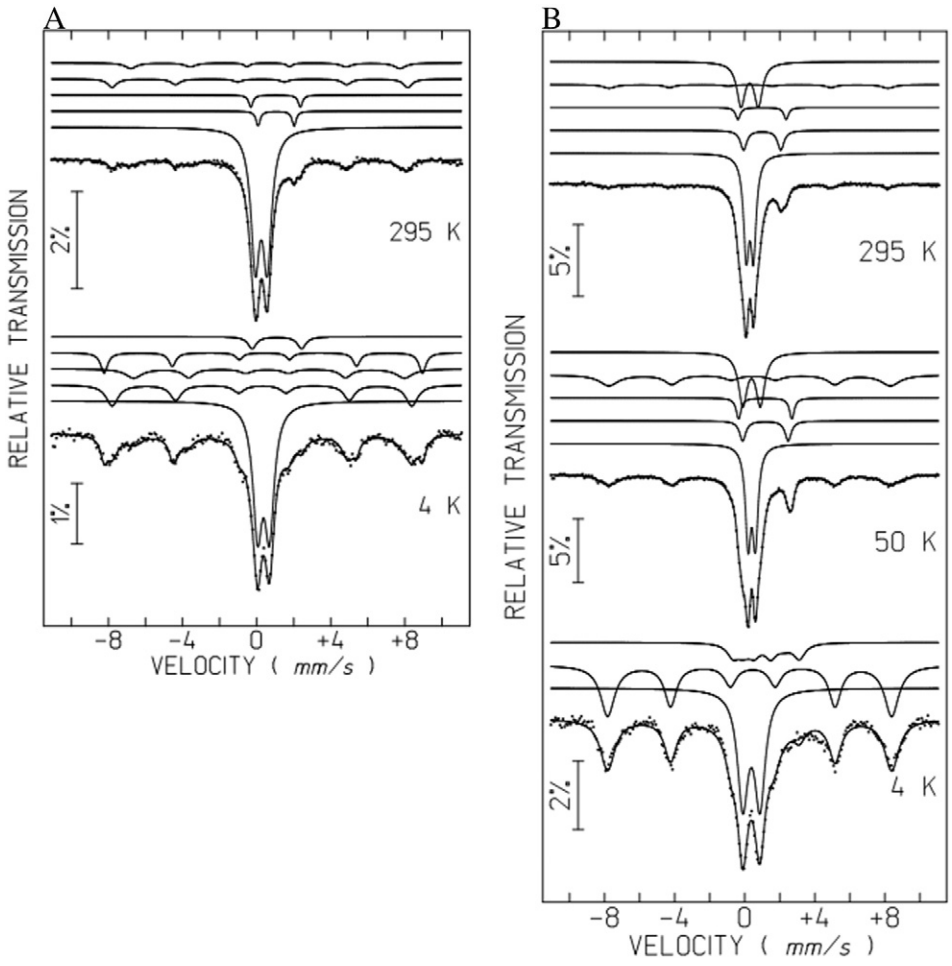

Fig. 7. Mössbauer spectra of: (A) 4-BRV topsoil (parent rock: phonolite crossed by carbonatite magmas); (B) 29-BRV topsoil (parent rock: sediment) from Brava (Cape Verde).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catena.2016.08.008.

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