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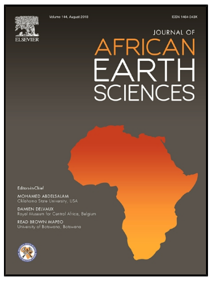

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Chemistry of volcanic soils used for agriculture in Brava Island (Cape Verde) envisaging a sustainable management

Rosa Marques[a*], Bruno J. Vieira[a], M. Isabel Prudêncio[a], João C. Waerenborgh[a], M. Isabel Dias[a], Fernando Rocha[b,c]

[a]Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, EN 10 (km 139.7), 2695-066 Bobadela, Portugal

[b]GeoBioTec, Universidade de Aveiro, Campus Universitário Santiago, 3810-193 Aveiro, Portugal

[c]Dep. de Geociências, Universidade de Aveiro, Campus Universitário Santiago, 3810-193 Aveiro, Portugal

* Corresponding author (rmarques@ctn.tecnico.ulisboa.pt)

brunovieira@ctn.tecnico.ulisboa.pt (Bruno J. Vieira)

iprudenc@ctn.tecnico.ulisboa.pt (M. Isabel Prudêncio)

jcarlos@ctn.tecnico.ulisboa.pt (João C. Waerenborgh)

isadias@ctn.tecnico.ulisboa.pt (M. Isabel Dias)

tavares.rocha@ua.pt (Fernando Rocha)

Abstract

In order to acquire a better knowledge of iron forms, clay minerals and the content and distribution of trace elements in soils mostly used for agriculture in the semi-arid Brava Island (Cape Verde), iron speciation, mineralogy and chemical contents in the clay-size fraction (< 2 μm) of incipient soils developed on sediments and phonolitic pyroclasts was performed by Mössbauer spectroscopy, X-ray diffraction and neutron activation analysis. In contrast with the whole samples in the clay-size fraction of all the studied soils only Fe(III) was detected. Iron and chromium are depleted suggesting their occurrence as ferromagnesian and oxide minerals present in coarser particles. Rare earth elements are concentrated in the clay-size fraction, and significant differences are found in their distribution which may be partially due to oxidation, since Ce anomalies were observed. Among the other chemical elements studied, high concentrations of arsenic, bromine, and particularly antimony were found in the clay-size fraction of soils where all the Fe oxides are nano-sized, confirming the predominant adsorption of these elements on the nano-particles surface. The existence of significant amounts of

these elements as well as of vitreous phases in fine particles of these soils may contribute to their mobility and accumulation in groundwater and in plants, both by absorption and by dust deposition onto the plant leaves.

Keywords: Brava Island; Cape Verde; Volcanic soil; REE; Trace elements; Iron speciation

1. Introduction

The knowledge of arid zone soils has become increasingly important since global warming has worsened the water resource crisis in many zones worldwide from Africa to Asia (Han, 2007). Volcanic eruptions form part of the biogeochemical cycle of the elements and represent one of the natural ways in which significant amounts of chemical elements enter the atmosphere (Nriagu, 1989). The environmental impact of ash deposits, which contribute with considerable quantities of metals to sediments and soils, is also of the utmost relevance. As shown by several studies, major, minor and trace elements can quickly transfer from ash into the environment, leading to considerably high concentration of these elements in water and vegetation (Cronin et al., 2003; Frogner et al., 2001; Jones and Gislason, 2008; Martin et al., 2009; Watt et al., 2009). Thus, soils with contribution from volcanic eruptions, particularly those developed on oceanic volcanic islands, may have significant amounts of a number of chemical elements. Volcanic soils are rich in mineral nutrients being amongst the most fertile lands in the world and are intensively cultivated. Nevertheless they may have an imbalance of chemical elements that can impact on the health of plants and animals growing in or on the soils (Neall, 2007). This may be particularly relevant in the case of volcanic islands of recent and contrasting volcanism that are under semi-arid climate, which is the case of Cape Verde.

The Cape Verde archipelago is located in the Atlantic Ocean. The semi-arid climate of these islands gives rise to topsoils with low to moderate degree of weathering and development, in general with less than 30 cm depth. Although Brava is one of the islands with more frequent rainy periods in Cape Verde, the aridity associated with the rough topography leads to incipient soils (Madeira and Ricardo, 2013). Nevertheless, soils of alluviums and colluviums, the major areas for agriculture, can be found in valleys. Furthermore, high contents of trace elements may occur originated from imbalance of elements in the volcanic parent materials, which may be a threat to the environmental health (Marques et al., 2012, 2014a, 2014b, 2016, 2017a, 2017b, 2017c). Detailed Fe speciation and chemical composition studies of Cape Verde soils, namely of Fogo and Brava Islands (Marques et al., 2014b, 2016, 2017c) have shown that oxidation is a major weathering mechanism. The global iron oxidation appears to be a good indicator of the weathering degree in these semi-arid islands. In addition to information on pedogenetic conditions Fe oxides may affect a number of soil properties, namely surface adsorption of numerous ions and molecules. Significant chemical content variations were found to occur as well as high contents of Mn, Co, Ga, Ba, rare earth elements (REE), Ta, W, Th and U in the whole sample ($\phi < 2$ mm) of soils (Marques et al., 2016). These results justify a more detailed study concerning fine particles, which have the highest surface areas, of soils used for agriculture in Brava, a crucial resource of this small island.

The soils mostly used for agriculture in Brava Island are those developed on phonolitic pyroclasts and sediments on a plateau between 300 and 976 m above sea level, and also on sediments occurring on terraces of fluvial incisions of the steep coastal cliffs (Fig. 1). In this work the clay-size fraction ($\phi < 2$ μm) of these soils were analysed by Mössbauer spectroscopy, X-ray diffraction and instrumental neutron activation analysis, in order to characterize the iron speciation, mineralogy and to determine the concentration and distribution of 29 chemical elements. Results are compared with those obtained for the corresponding whole samples (Marques et al., 2016).

The main objectives of this work are therefore: (1) the chemical characterization of the clay-size fraction of the surficial layer of soils developed on sediments and phonolitic pyroclasts in Brava Island (Cape Verde); (2) the iron distribution in mineralogical phases of the clay-size fraction of the soils; (3) the assessment of the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio; and (4) the establishment of the geochemical patterns and the identification of chemical elements with high contents. Thus a better knowledge of soils used for agriculture in Brava Island is a major motivation of this work, contributing for the identification of potential risks to humans coupled with the need of the population of this island to produce food.

2. Geological setting, climate and study area

The Cape Verde archipelago is composed of 10 islands and several islets, and is located 600 to 900 km west of the African coast, on the southwestern part of the Cape Verde Rise (Fig. 2A). Generally moderate, the climate of Cape Verde islands is characterized by stable temperatures with extreme aridity. Precipitation levels are unpredictable, depending on how the intertropical convergence zone (ITCZ) progresses and how much tropical moisture it carries. Years may pass with little or no precipitation. Marine and fluvial erosion and mass wasting processes have contributed to the present morphology of the Brava 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).

3. Materials and methods

The soils of Cape Verde archipelago are mainly inceptisols and entisols on basaltic substrate with low organic matter, mainly of volcanic origin, and shallow (circa 30 cm depth) with a low water holding capacity (Madeira and Ricardo, 2013). Field work and sampling was performed in 2013 in Brava Island (see Fig. 2B). Sampling of nine surficial layer of the soils (0-20 cm depth), hereafter referred to as topsoils, was performed: six developed on sediments and three on phonolitic pyroclasts (Upper Unit). A wide variety of vegetables (like sweet potato, beans, corn, cabbage, carrots, etc), and fruits (banana, mango, papaya, etc) are cultivated in this island. The irrigation of crops is dependent of rainfall regime, but nowadays the drip irrigation system has been implemented in Brava. The sample reference, UTM coordinates, altitude, granulometry, color, and geological unit/parent rock according to Madeira et al. (2010) are given for each soil (Table 1).

The clay-size fraction of each topsoil was obtained as follows: circa 100 g of the $\phi < 50$ μm fraction resulting from wet sieving with deionized water (nylon mesh) was used to obtain the $\phi < 2$ μm fraction by sedimentation according to Stokes' law (Moore and Reynolds, 1997) after dispersion with sodium hexametaphosphate (1%).

The mineralogical composition of the clay-size fraction was determined by X-ray diffraction (XRD) of oriented specimens on glass slides using a Philips diffractometer, Pro Analytical, with Cu Kα radiation at 40 kV and 35 mA within the 2° - 30° 2θ range, with a step size of 1° 2θ/min. The following treatments were performed: air drying, ethylene glycol solvation (EG), and heating (550 °C). The minerals identification was done according to Brindley and Brown (1980), Moore and Reynolds (1997), Thorez (1976) and Trindade et al. (2011).

Chemical elements concentrations 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. Corrections for the spectral interference from U fission products in the determination of Ba, REE and Zr were made according to Gouveia et al. (1987) and Martinho et al. (1991), and more details of the analytical method may be found in Marques et al. (2011) and Prudêncio et al. (2006, 2015). Relative precision and accuracy are, in general, to within 5%, and occasionally within 10%.

The ^{57}Fe Mössbauer measurements were recorded at 295 and 4 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 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. The measurements taken at 4 K were obtained with the samples immersed in liquid He in a bath cryostat. The spectra were fitted to Lorentzian lines using a non-linear least-squares method (Waerenborgh et al., 1990).

4. Results

The XRD results for the clay-size fraction of topsoils from Brava Island (Cape Verde) showed the existence of a significant vitreous component, evidenced by a bulge in the baseline of the diffractograms and a low proportion of clay minerals crystalline phases. The clay minerals identified in topsoils developed on sediments and phonolitic pyroclasts are:

- Sediments – illite, kaolin minerals and traces of chlorite and mixed-layer illite/smectite (I/Sm) in all samples; in addition smectite was also identified in the topsoils developed on a slope talus (7-BRV) and on a landslide deposit (8-BRV), both located on the western part of the island with contributions from the Lower Unit and the Upper Unit (see Fig. 2B).

- Phonolitic pyroclasts – illite associated to traces of kaolin minerals, mixed-layer I/Sm and chlorite.

The chemical results obtained by INAA for the clay-size fraction of the topsoils are given in Table 2. Significant variations were found for the studied chemical elements (in increasing order): $c < 30\%$ for Fe, Ga, Cr, Rb, W and Cs; $30\ \% \leq c \leq 50\ \%$ for As, K, Mn, U, Ta, Zn, Br, Sc, Lu, Yb, Th and Co; $c > 50\ \%$ for Tb, Ba, Zr, Sm, Na, Eu, Hf, Ce, Nd, La and Sb. Arsenic, U and particularly Zn concentrations may differentiate soils developed on sediments and on phonolitic pyroclasts, being lower on sediments, even on soil 2-BRV which corresponds to an alluvium with a major contribution from the Upper Unit.

Mössbauer spectra (Fig. 3) of all the samples taken at room temperature consist of one doublet. The estimated parameters for these doublets, summarized in Table 3, are typical of Fe^{3+} (Greenwood and Gibb, 1971). At 4 K all the spectra (Fig. 4) show in addition to the doublet six broad absorption peaks which were analyzed by two magnetic sextets.

4.1. Rare earth elements patterns

The rare earth elements (REE) patterns of the clay-size fraction of topsoils developed on sediments and on phonolitic pyroclasts relative to chondrites, and to the corresponding whole sample (data from Marques et al., 2016) are shown in Fig. 5A and 5B, respectively.

- Sediments - the lowest REE contents, fractionation between light REE (LREE) and heavy REE (HREE) ($(La/Yb)_{ch}$ = 15), and a positive Ce anomaly (Ce/Ce*= 1.2) were found in topsoils 7-BRV and 8-BRV, located in the western part of the island with contributions from the Lower Unit and the Upper Unit (Fig. 5A); in the alluvium deposits located in the plateau with a major contribution from the Upper Unit (samples 2-BRV and 32-BRV) similar REE contents and patterns were found, except for higher LREE contents, particularly La, originating a higher LREE/HREE ratio ($(La/Yb)_{ch}$ = 35) in the sample 32-BRV, located close to the Minhoto Fault Zone (MFZ); the highest REE contents were found in alluvium deposits (28-BRV and 29-BRV) in the southern part of the island with contributions from the Middle and the Upper Unit. A negative Ce anomaly also occurs (Ce/Ce* = 0.7). Comparing the REE in the clay-size fraction with the respective whole sample (Fig. 5B), the LREE and HREE are in general more enriched than the middle REE (MREE). A positive Ce anomaly occurs, particularly in the topsoils developed on sediments of the western part the island (7-BRV, 8-BRV) and in the alluvium deposit of the bottom of a crater in the southern part of the plateau (2-BRV).

- Phonolitic pyroclasts – REE patterns relative to chondrites (Fig. 5C) show a slight negative Ce anomaly (Ce/Ce* = 0.6–0.8). The sample collected near the MFZ has the highest REE contents and fractionation ($(La/Yb)_{ch}$ = 71). The remaining topsoils present similar contents and patterns. When compared to the respective whole sample (Fig. 5D), the two topsoils located near the MFZ (18-BRV and 31-BRV) show a similar pattern with a negative Ce anomaly.

4.2. Other chemical elements

The distribution patterns of the other chemical elements in the clay-size fraction relative to the corresponding whole sample are shown in Fig. 6.

- Sediments – a general depletion of Fe and Cr is observed; Na and K are also depleted except in sample 7-BRV (talus deposit). An enrichment of Mn, As, Br, Sb, W and Th occurs in the clay-size fraction of all studied topsoils; the same tendency is observed for Zn, except in sample 2-BRV (alluvium in the bottom of a crater). The topsoils developed on the sediments located in the southern part of the island (28-BRV and 29-BRV) with major contributions from the Middle and Upper Unit, can be distinguished by the highest depletion of Fe, Ga, Rb, Zr, Hf, Ta, and U in the clay-size fraction (Fig. 6A).

- Phonolitic pyroclasts – Fe, Cr, Rb, and Ba are depleted in the clay-size fraction of the three topsoils studied; Zn, As, Br, Sb and Th are enriched (Fig. 6B). Arsenic, Br and particularly Sb can be strongly enriched (up to 70 times) in the clay-size of topsoils developed on both sediments and phonolitic pyroclasts.

5. Discussion

The doublet and sextets observed in Mössbauer spectra at 4 K of the clay-size fraction of Brava Island soils correspond to contributions from different Fe-bearing phases, as explained in detail in Marques et al. (2014b) the doublet may be assigned to Fe^{3+} in the silicate phases and the sextets to Fe^{3+} oxides (Murad, 1998). All these oxides are nano-sized since at room temperature no sextets are observed. The poor crystallinity (small crystal size, unspecific particle shape, structural disorder) and Fe^{3+} isomorphous substitution by impurity cations such as Al^{3+} give rise to a range of isomer shifts, quadrupole interactions and magnetic hyperfine fields (Murad, 1998; Vandenberghe et al., 2000). This range of parameter values may explain the significant peak broadening that prevents the clear identification of resolved contributions from different oxides, namely hematite or maghemite which were detected in the whole fraction of these samples (Marques et al., 2016). In summary, Mössbauer spectroscopy shows that in the clay-size fraction of the studied topsoils all the Fe is present as Fe^{3+} and all the Fe oxides are nano-sized independently of the topsoils weathering degree deduced from the analysis of the whole samples (Marques et al., 2016).

As far as REE are concerned, the relative Ce enrichment observed in the clay-size fraction of some of the studied sediments (2-BRV, 7-BRV and 8-BRV) indicates stronger oxidizing conditions leading to $Ce^{3+} \rightarrow Ce^{4+}$ with preferred retention of this element on the clay-size particles when compared to the other LREE. Sample 2-BRV also has the highest fraction of Fe in nano-sized oxides (Table 3). This is consistent with the Ce behavior, assuming that nano-sized Fe oxides may be the Fe-containing end-products of weathering. A negative Ce anomaly is observed in the alluvium sediments located in the south of the island with contributions from the Middle Unit and the Upper Unit, mainly due to high La contents in the fine particles (28-BRV, 29-BRV). In these samples a negative Eu anomaly is also observed suggesting the preferential presence of this element in the coarser particles (see Fig. 5B).

Thus, REE contents and patterns in the clay-size fraction of all studied samples appear to depend on the composition of the parent rock of the topsoils. Regardless of the general enrichment of the REE in the clay-size fraction found both in sediments and phonolitic pyroclasts, significant differences occur in the concentrations and distribution relative to the corresponding whole sample, which may reflect distinct oxidizing conditions as the Ce anomaly suggests; eventual contributions of fine particles resulting from volcanic activities, particularly close to MFZ that crosses the island in a NE-SW direction, may also play an important role.

Among the other chemical elements determined in the clay-size fraction of soils, the depletion of Fe and Cr on sediments suggest their occurrence as iron oxides and ferromagnesian minerals present in coarser particles. When the whole samples of both sediments and phonolitic pyroclasts of Brava Island were studied (Marques et al., 2016) a correlation was found between the concentration of As, Br and Sb and the oxidation degree of Fe. The present data, showing that these elements are enriched in the clay-size fraction where all the Fe oxides are nano-sized, confirms the predominant adsorption of As, Br and Sb on these nano-particles surface. Despite the general low contents of these trace elements, their presence in fine particles of soils from Brava Island consisting of poorly crystallized clay and oxide phases as well as vitreous phases may contribute for their mobility and accumulation in plants, and in groundwater. Also dust deposition onto the plant leaves should be considered as potential risks to the local population using these soils for agriculture to produce food. All the Fe^{2+} detected in the whole samples of topsoils (Marques et al., 2016), most of it within the silicate structures, is present in the coarser fraction of the samples since no Fe^{2+} is detected in the clay-size fraction. This may be related to the lower Fe content of the clay-size fraction when compared to the whole sample. Sediment samples 28-BRV and 29-BRV have very similar Fe speciation and chemical composition both when analyzed as whole samples (Marques et al., 2016) and as clay-sized fraction. All the other soils which have similar chemical compositions have significantly different fractions of Fe in nano-oxides (for instance 2-BRV and 32-BRV, or 31-BRV and 40-BRV).

Considering the geographical proximity of 28-BRV and 29-BRV they seem to be soils developed on the same sedimentary formation in similar conditions during the depositional event, and to have suffered similar weathering processes during the same time span.

6. Conclusions

The elemental distribution in the clay-size fraction of the surficial layer of soils developed on sediments and on phonolitic pyroclasts in Brava Island (Cape Verde) show significant chemical content variations, particularly for Fe, Ga, Cr, Rb, W and Cs. A general enrichment of REE in the clay-size fraction relative to the whole sample is observed in both soils developed on sediments and phonolitic pyroclasts. Nevertheless, significant differences are found in REE concentration and distribution which may be partially due to weathering, since different oxidizing conditions are suggested by the Ce anomalies. Iron and chromium are depleted. All the iron in the clay-size fraction of the topsoils is present as Fe^{3+} pointing to oxidation as the main chemical weathering mechanism. The iron oxides in the clay-size fraction are nano-sized. Among the chemical elements studied, the most enriched in the clay-size fraction are As, Br and especially Sb. Considering the positive correlation found for the whole samples between the iron oxidation degree and the concentration of these elements (Marques et al., 2016) they are most likely adsorbed onto the Fe oxides nano-particles surface as well as in poorly crystalline clay minerals. In spite of the low contents of As, Br and Sb their presence on nano-sized particles and in a significant vitreous component in the clay-size fraction of these soils contributes for their mobility and distribution in the biogeochemical cycles having a potential impact on the agriculture in Brava Island.

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Figure Captions

Fig. 1. Photographs of Brava Island (Cape Verde) with a view to agriculture soils developed on (A) phonolitic pyroclasts (Nova Sintra), and (B) terrace sediments (Tantum).

Fig. 2. A) Location of Brava Island in the Cape Verde archipelago, and B) Sampling location of nine studied topsoils of the Brava Island (superposed to the Brava geological map by Madeira et al. (2010)).

Fig. 3. Mössbauer spectra taken at 295 K of the clay-size fraction of three topsoils. The lines over the experimental points are doublets corresponding to Fe^{3+}. The estimated parameters for these doublets, shown slightly shifted for clarity, are collected in Table 2.

Fig. 4. Mössbauer spectra taken at 4 K of the clay-size fraction of topsoils from Brava Island (Cape Verde): A) five topsoils developed on sediments; and B) three topsoils developed on phonolitic pyroclasts. The lines over the experimental points are the sum of a doublet and two sextets corresponding to Fe^{3+} in silicates and nano-sized oxides, respectively. The estimated parameters for these doublet and sextets, shown slightly shifted for clarity, are collected in Table 2.

Fig. 5. REE patterns of the clay-size fraction of topsoils from Brava Island relative to chondrites (values of Anders and Grevesse (1989) multiplied by 1.36 according Korotev (1996a, 1996b)) and to the respective whole samples: A) and B) soils developed on sediments; and C) and D) soils developed on phonolitic pyroclasts.

Fig. 6. Trace element distribution in the clay-size fraction relative to the respective whole sample of soils from Brava Island: A) developed on sediments and B) developed on phonolitic pyroclasts.

Table Captions

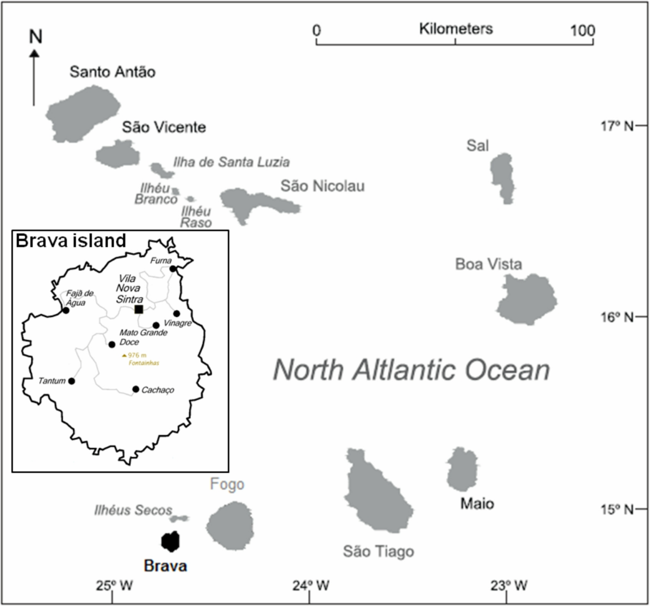
Table 1. Geological unit/parent rock, sample references, UTM coordinates (m), altitude (m), granulometry and color of topsoils from Brava Island (Cape Verde).

Table 2. Sample references, and chemical composition of the clay-size fraction of topsoils from Brava Island (Cape Verde).

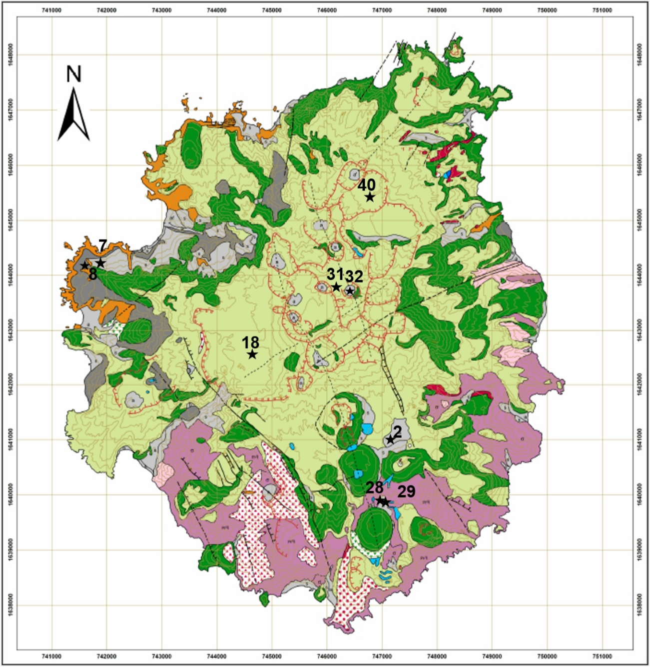
Table 3. Estimated parameters from the Mössbauer spectra, taken at different temperatures, of the clay-size fraction of Brava Island topsoil samples.

Highlights

- REE enrichment in the clay-size fraction of sediments and phonolitic pyroclast soils
- High concentrations of As, Br and especially Sb in clay-size fraction
- Predominant adsorption of As, Br and Sb on nano-sized iron oxide particles surfaces
- Only Fe(III) occurs in clay-size fraction of the topsoils
- All the Fe oxides occurring in the fine fractions are nano-sized



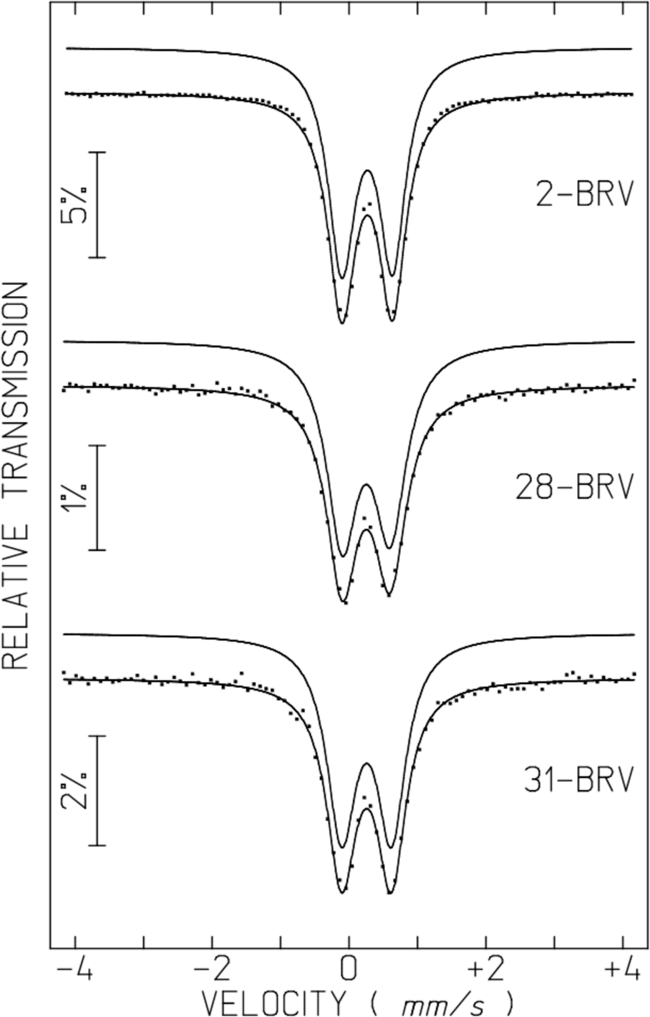
N
0
Kilometers
100
Santo Antão
São Vicente
Ilha de Santa Luzia
Ilhéu Branco
Ilhéu Raso
São Nicolau
Sal
17º N
Boa Vista
16º N
Brava island
Furna
Vila Nova Sintra
Fajã de Água
Vinagre
Mato Grande
Doce
976 m Fontainhas
Tantum
Cachaço
North Altlantic Ocean
Fogo
Ilhéus Secos
Brava
São Tiago
Maio
15º N
25º W
24º W
23º W



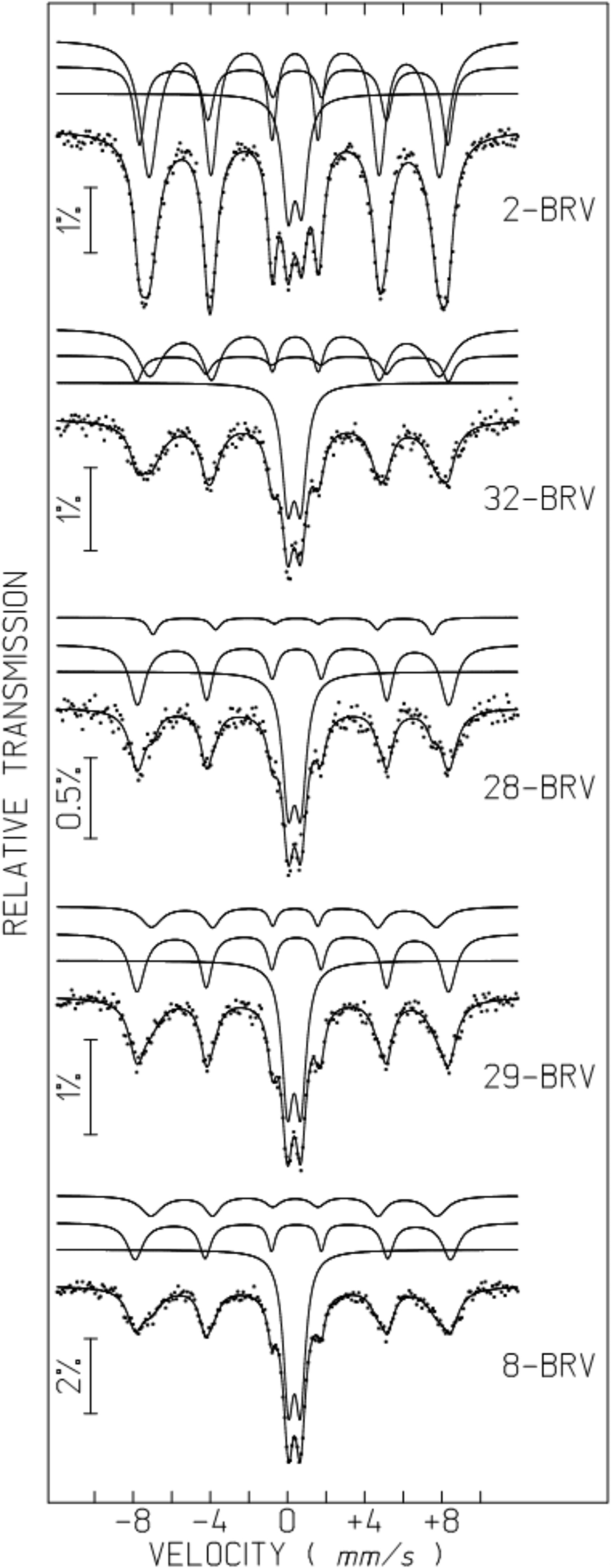
1:25 000 Scale

0.5 0.25 0 0.5 1 1.5 2 kilometres

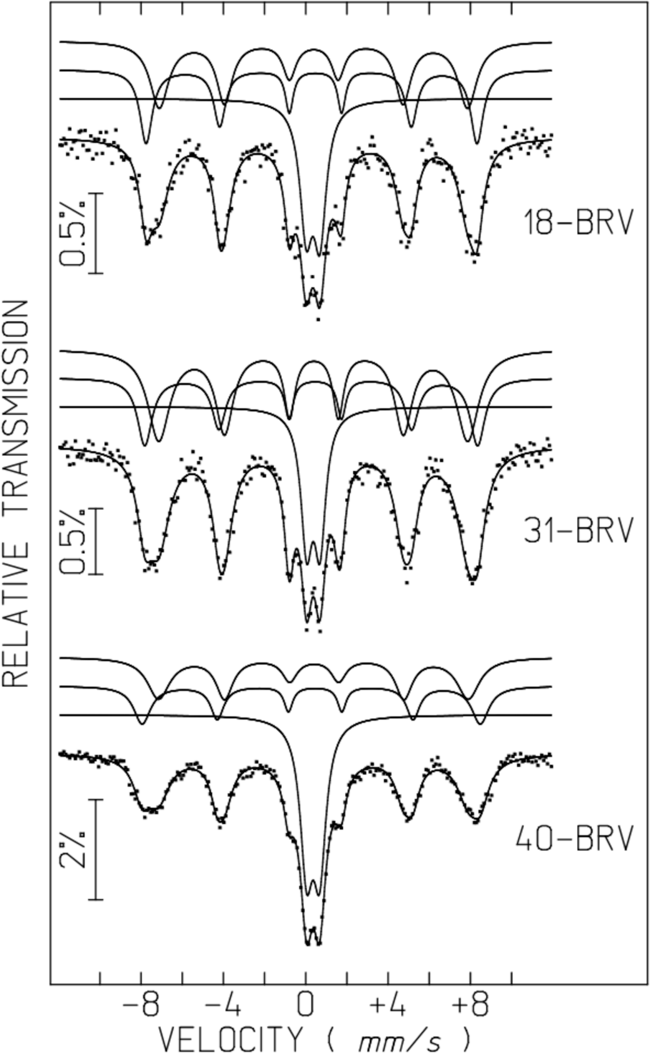
Contour interval of 50 meters

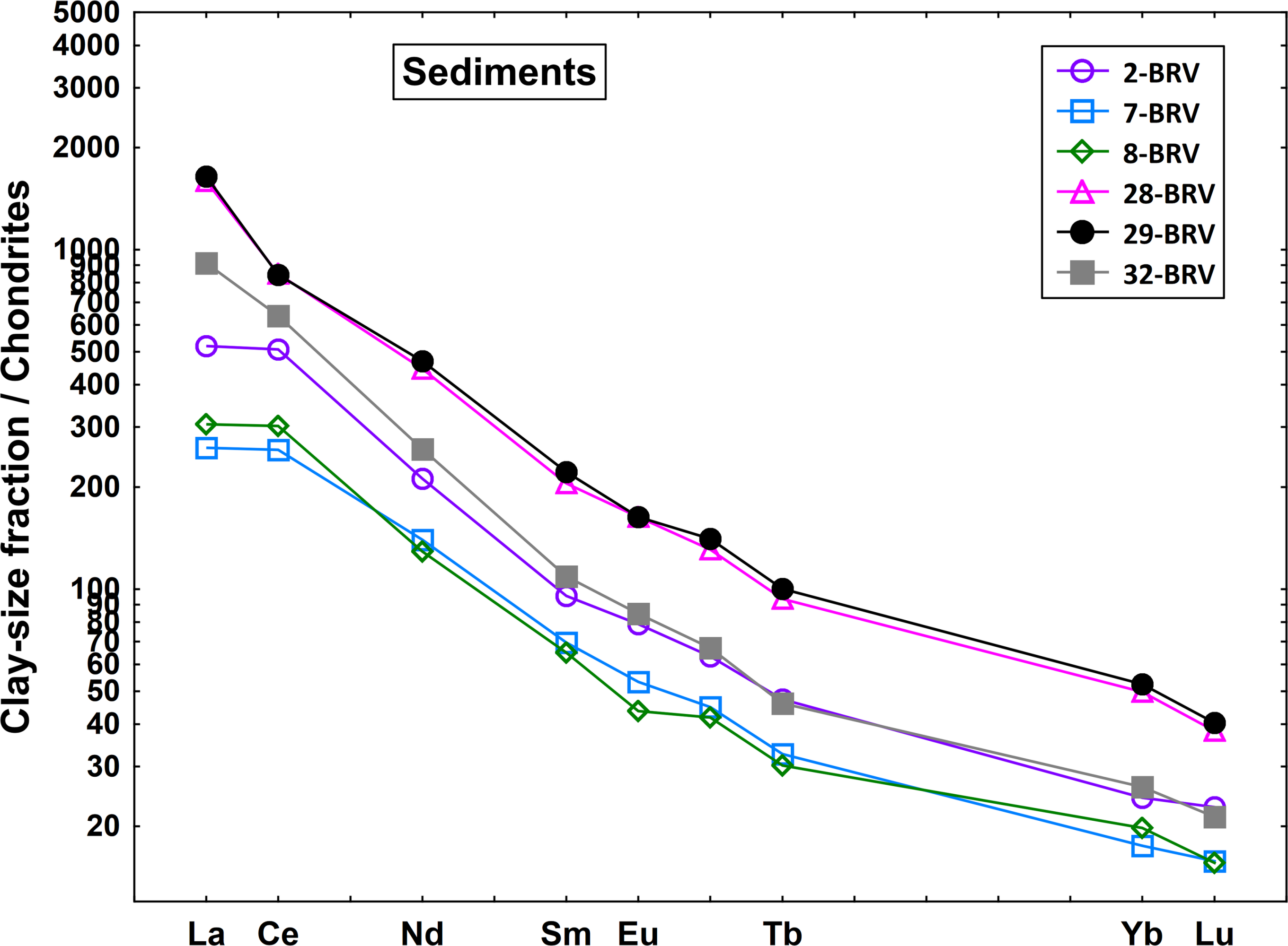


RELATIVE TRANSMISSION
5%
2-BRV
1%
28-BRV
2%
31-BRV
-4
-2
0
+2
+4
VELOCITY (mm/s)

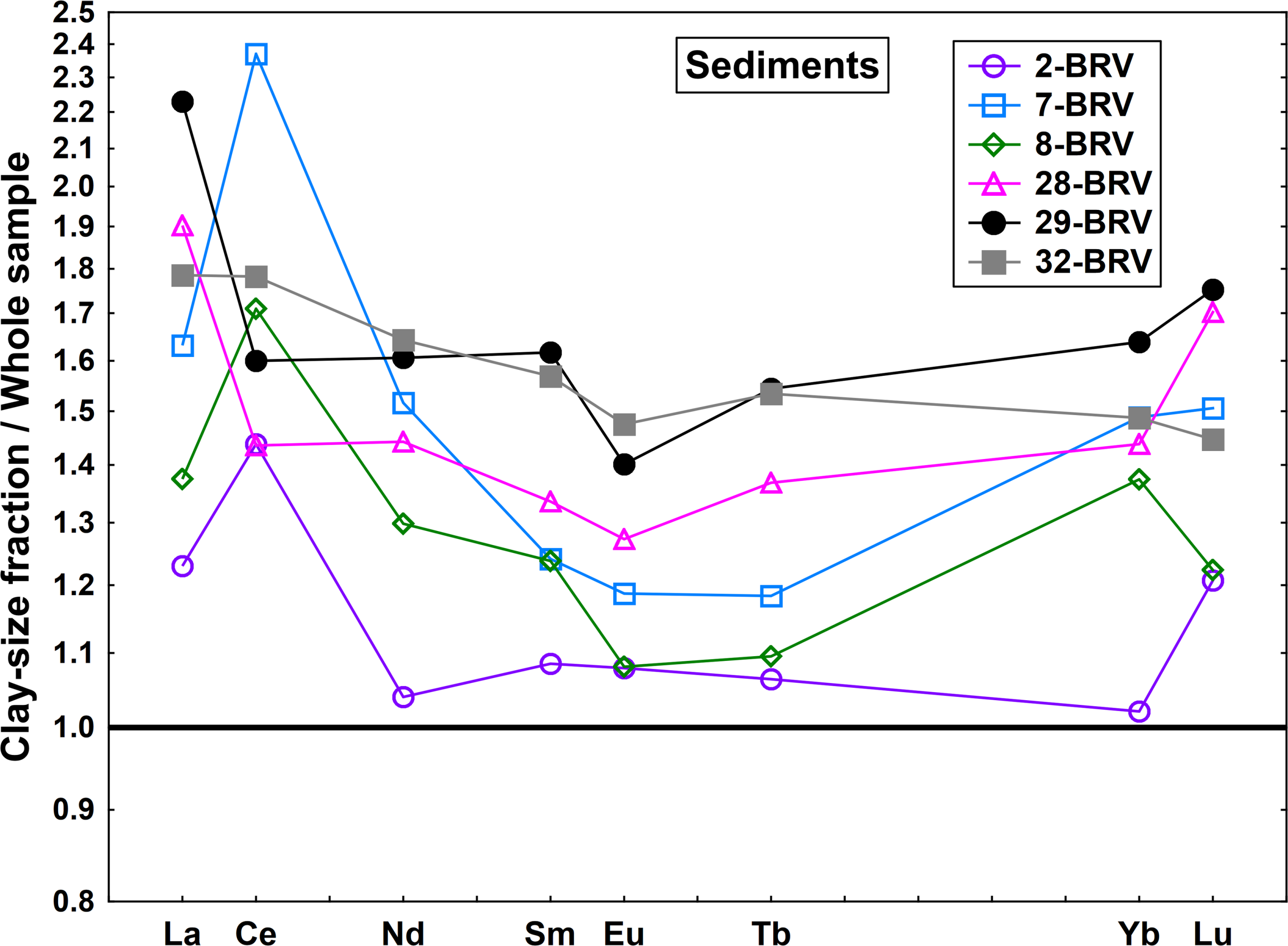


RELATIVE TRANSMISSION
1%
2-BRV
1%
32-BRV
0.5%
28-BRV
1%
29-BRV
2%
8-BRV
-8
-4
0
+4
+8
VELOCITY (mm/s)

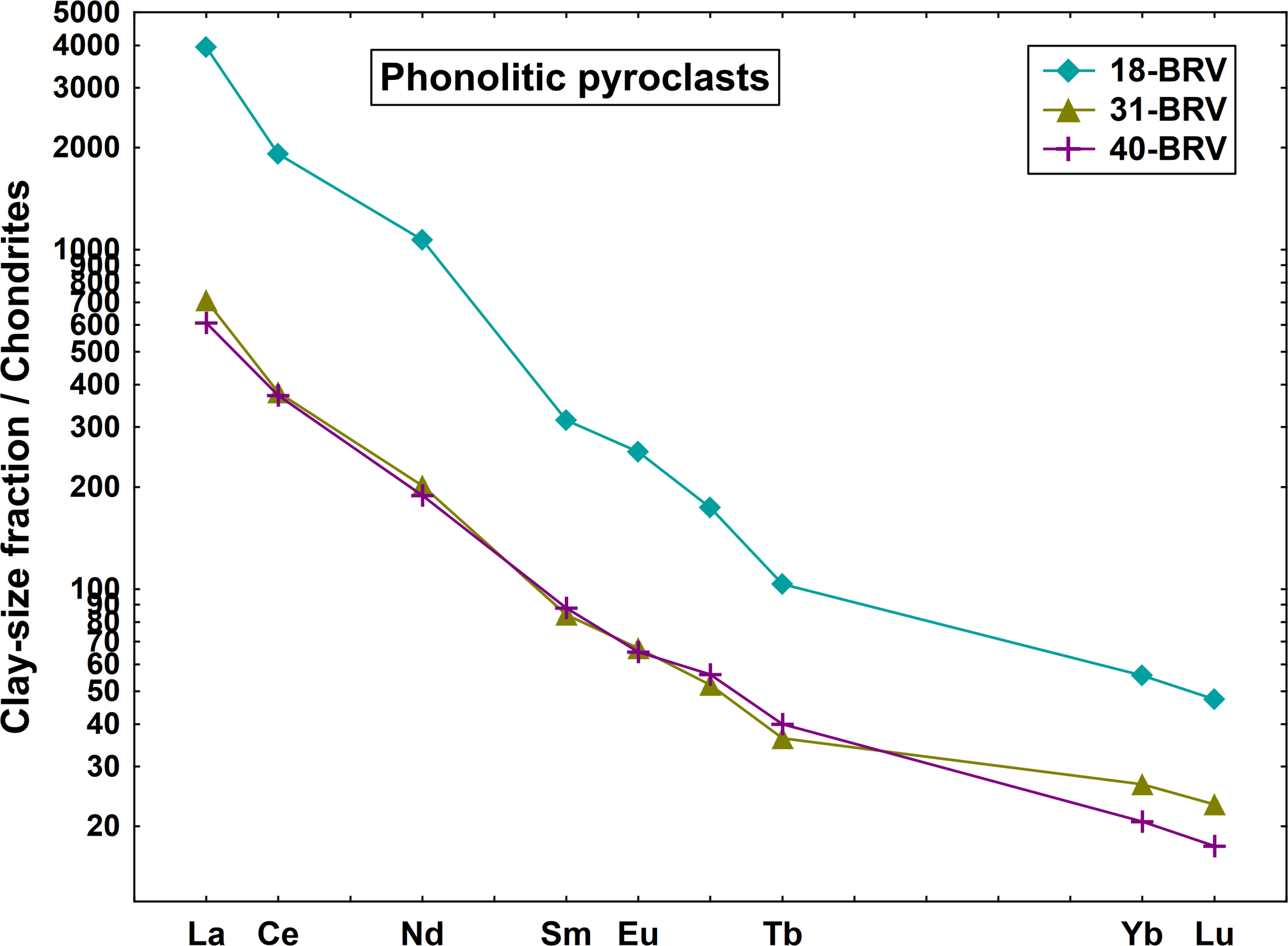

RELATIVE TRANSMISSION
0.5%
18-BRV
0.5%
31-BRV
2%
40-BRV
-8
-4
0
+4
+8
VELOCITY (mm/s)

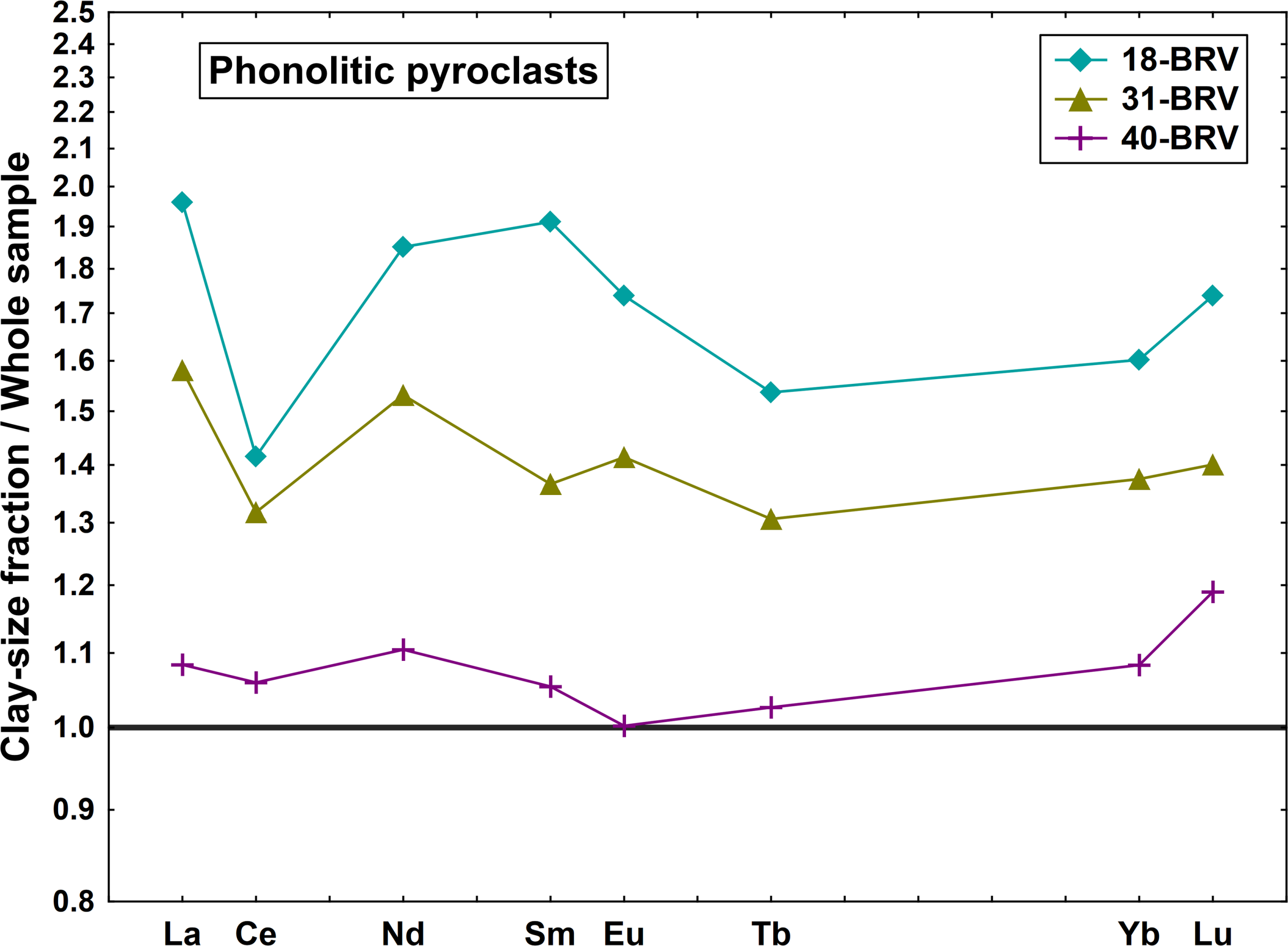


Sediments
2-BRV
7-BRV
8-BRV
28-BRV
29-BRV
32-BRV
Clay-size fraction / Chondrites
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu

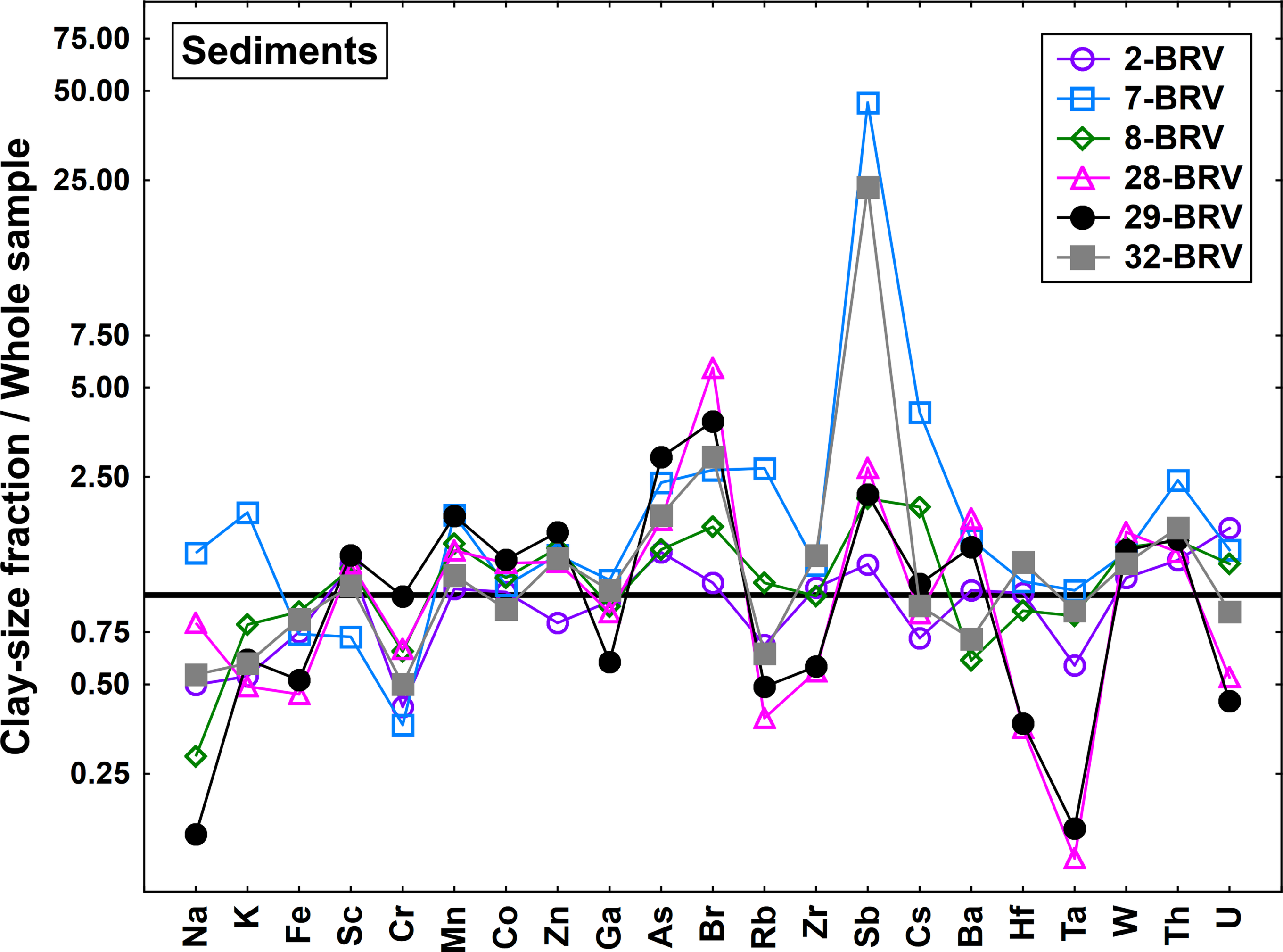


Sediments
2-BRV
7-BRV
8-BRV
28-BRV
29-BRV
32-BRV
Clay-size fraction / Whole sample
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu

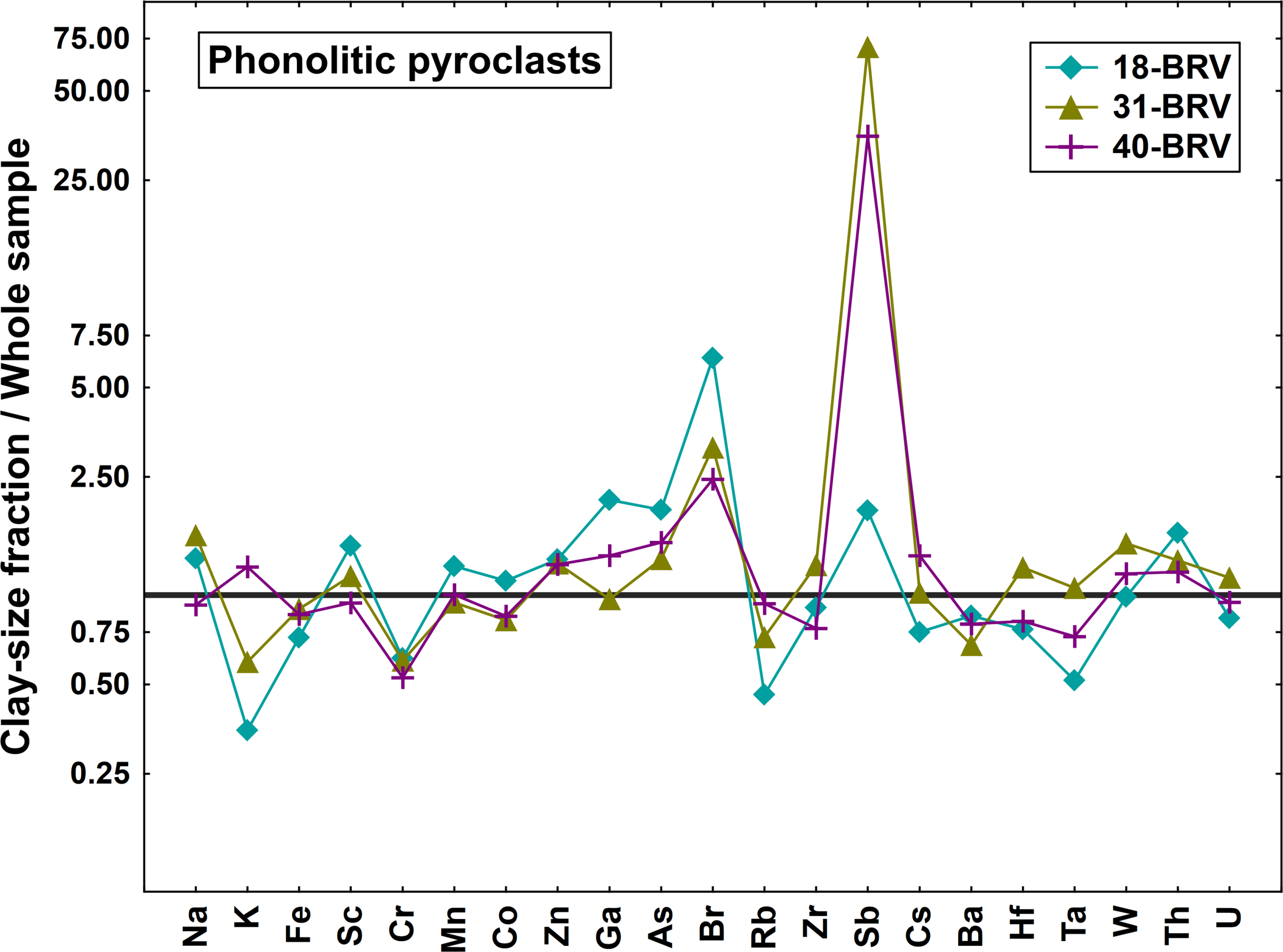

Phonolitic pyroclasts
18-BRV
31-BRV
40-BRV
Clay-size fraction / Chondrites
5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu



Phonolitic pyroclasts
18-BRV
31-BRV
40-BRV
Clay-size fraction / Whole sample
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu



Sediments
2-BRV
7-BRV
8-BRV
28-BRV
29-BRV
32-BRV
Clay-size fraction / Whole sample
75.00
50.00
25.00
7.50
5.00
2.50
0.75
0.50
0.25
Na
K
Fe
Sc
Cr
Mn
Co
Zn
Ga
As
Br
Rb
Zr
Sb
Cs
Ba
Hf
Ta
W
Th
U



Phonolitic pyroclasts
18-BRV
31-BRV
40-BRV
Clay-size fraction / Whole sample
75.00
50.00
25.00
7.50
5.00
2.50
0.75
0.50
0.25
Na
K
Fe
Sc
Cr
Mn
Co
Zn
Ga
As
Br
Rb
Zr
Sb
Cs
Ba
Hf
Ta
W
Th
U

Table 1. Geological unit/parent rock, sample references, UTM coordinates (m), altitude (m), granulometry and color of topsoils from Brava Island (Cape Verde).

Geological Unit	**Sediments**					**Upper Unit**			
Parent rock	**Alluvium**	**Slope tallus**	**Landslide deposits**	**Alluvium**	**Alluvium**	**Phonolitic pyroclasts**	**Phonolitic pyroclasts**	**Phonolitic pyroclasts**	**Phonolitic pyroclasts**
Field Reference	**2-BRV**	**7-BRV**	**8-BRV**	**28-BRV**	**29-BRV**	**18-BRV**	**31-BRV**	**32-BRV**	**40-BRV**
X	747105	741894	741631	746947	747053	744631	746158	746421	746789
Y	1641368	1644210	1644210	1639789	1639736	1642579	1643684	1643736	1645421
Altitude	600	80	50	430	430	650	790	780	475
Granulometry $\phi < 50$ µm (%)	60.0	22.0	44.0	20.0	20.0	26.0	67.0	46.0	57.0
Munsell Color (Munsell, 1998)	Yellowish red 5 YR (4/6)	Dark Yellowish brown 10 YR (4/4)	Dark Yellowish brown 10 YR (3/4)	Dark Yellowish brown 10 YR (4/4)	Dark Yellowish brown 10 YR (4/4)	Brown 7.5 YR (4/4)	Dark Yellowish brown 10 YR (4/6)	Yellowish brown 10 YR (5/4)	Brown 7.5 YR (4/4)

Table 2. Sample references, and chemical composition of the clay-size fraction of topsoils from Brava Island (Cape Verde).
(major elements in % w/w, and trace elements in mg/kg)

Field Reference (size fraction)	2-BRV (< 2 µm)	7-BRV (< 2 µm)	8-BRV (< 2 µm)	28-BRV (< 2 µm)	29-BRV (< 2 µm)	18-BRV (< 2 µm)	31-BRV (< 2 µm)	32-BRV (< 2 µm)	40-BRV (< 2 µm)
Na_2O	0.418	0.743	0.446	1.88	0.356	2.37	2.02	1.32	1.25
K_2O	1.14	2.26	2.49	1.56	1.63	1.61	2.22	2.32	3.44
Fe_2O_3T	11.1	12.1	10.1	5.93	6.10	8.99	8.69	7.92	9.30
Sc	20.6	21.9	21.0	6.47	7.08	11.5	12.3	11.1	16.1
Cr	34.5	54.1	69.8	40.8	50.0	41.8	52.5	40.5	64.3
Mn	2742	2927	3477	4662	5615	7489	3291	3501	4236
Co	36.9	64.0	42.4	25.4	24.9	19.0	17.6	17.7	27.5
Zn	124	209	305	332	376	588	387	335	518
Ga	35.2	28.4	30.4	45.5	27.4	49.6	50.6	41.7	38.1
As	4.87	4.90	4.97	2.81	3.53	7.65	6.98	4.81	4.50
Br	22.3	36.7	36.5	26.0	17.2	27.3	62.8	30.4	33.2
Rb	65.0	91.8	123	66.2	77.5	117	121	108	102
Zr	673	462	463	402	441	783	1699	1010	333
Sb	0.288	12.5	0.487	0.319	0.334	0.530	28.1	6.50	14.3
Cs	1.58	3.00	4.36	2.52	2.86	3.32	4.81	3.05	3.71
Ba	1703	439	521	1989	1476	2484	737	1021	895
La	166	83.2	97.6	508	524	1260	226	291	194
Ce	417	211	248	696	691	1568	311	524	305
Nd	130	85.8	79.2	274	289	657	124	159	116
Sm	19.1	13.9	13.0	41.0	44.3	62.9	16.8	21.8	17.6
Eu	6.00	4.06	3.33	12.4	12.4	19.3	5.09	6.43	4.97
Tb	2.33	1.61	1.49	4.61	4.94	5.10	1.79	2.27	1.97
Yb	5.37	3.87	4.37	11.0	11.6	12.3	5.87	5.77	4.56
Lu	0.751	0.521	0.515	1.26	1.33	1.56	0.766	0.703	0.577
Hf	13.4	8.12	8.74	4.52	4.80	10.2	28.0	17.3	6.94
Ta	4.52	4.40	4.51	1.80	2.24	2.96	7.10	5.03	3.78
W	2.79	2.17	3.15	5.05	4.08	4.05	4.14	3.32	2.61
Th	18.4	11.7	15.4	18.7	19.9	48.3	34.3	28.5	16.4
U	2.49	2.61	2.97	3.87	3.23	5.98	6.37	3.60	3.36

Table 2. Estimated parameters from the Mössbauer spectra, taken at different temperatures, of the clay-size fraction of Brava Island topsoil samples.

Sample reference	T		IS, mm/s	QS, ε, mm/s	B_{hf} , tesla	Γ, mm/s	I	$\%Fe_{nso}$
2-BRV	295 K	Fe^{3+} nso/silicate	0.38	0.74	-	0.48	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.50 0.52 0.49	0.71 -0.19 -0.04	- 49.5 46.6	0.74 0.63 0.57	15% 23% 62%	85%
8-BRV	295 K	Fe^{3+} nso/silicate	0.36	0.66	-	0.55	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.47 0.48 0.48	0.63 -0.19 -0.07	- 50.7 46.0	0.65 0.45 0.90	41% 34% 25%	59%
28-BRV	295 K	Fe^{3+} nso/silicate	0.37	0.70	-	0.55	100%	
		Fe^{3+} silicate Fe^{3+}nso	0.47 0.50 0.48	0.65 -0.19 -0.20	- 50.0 44.9	0.72 0.62 0.61	38% 53% 9%	62%
29-BRV	295 K	Fe^{3+} nso/silicate	0.37	0.69	-	0.56	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.46 0.48 0.48	0.69 -0.19 -0.06	- 50.1 45.8	0.69 0.56 0.49	36% 44% 20%	64%
32-BRV	295 K	Fe^{3+} nso/silicate	0.37	0.72	-	0.52	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.46 0.47 0.50	0.68 -0.20 -0.04	- 50.0 46.5	0.73 0.73 0.68	30% 14% 56%	70%
18-BRV	295 K	Fe^{3+} nso/silicate	0.37	0.70	-	0.53	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.47 0.49 0.49	0.67 -0.19 -0.02	- 49.9 46.4	0.75 0.46 0.77	26% 31% 43%	74%
31-BRV	295 K	Fe^{3+} nso/silicate	0.37	0.73	-	0.53	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.48 0.48 0.49	0.65 -0.20 -0.03	- 50.1 46.5	0.68 0.51 0.64	20% 26% 54%	80%
40-BRV	295 K	Fe^{3+} nso/silicate	0.38	0.72	-	0.57	100%	
	4 K	Fe^{3+} silicate Fe^{3+}nso	0.47 0.47 0.50	0.63 -0.19 -0.04	- 50.9 46.7	0.75 0.51 0.88	36% 26% 39%	64%

nso – nanosized Fe oxides which are superparamagnetic at room temperature

$\%Fe_{nso}$ fraction of the total Fe in the topsoil incorporated in Fe^{3+} oxides

IS (mm/s) – isomer shift relative to α-Fe at 295 K; QS (mm/s) – quadrupole splitting and ε (mm/s) – quadrupole shift estimated for quadrupole doublets and magnetic sextets, respectively.

B_{hf} (tesla) – magnetic hyperfine field; I – relative area. Estimated errors are ≤ 0.02 mm/s for IS, QS, ε, < 0.2 T for B_{hf} and < 2% for I.