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REE and other trace and major elements in the topsoil layer of Santiago island, Cape Verde

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ABSTRACT

Geochemistry of major, trace and rare earth elements (REEs) of soils of Santiago island (Cape Verde) has been done in order to characterize soils developed on volcanic rocks and Quaternary sediments, contributing to the establishment of a geochemical atlas of the island. Sampling was made according to the recommendations of the IGCP 259 ("International Geochemical Mapping"). REE clearly differentiate soils with contrasting parent materials, particularly carbonatites-related soils, where lower MREE/LREE and MREE/HREE ratios were found, associated with higher contents of Ba, Th and U. Total contents of Cs, As and Ga are associated with the finer soils. The percentage of Fe, Co, Mn and Sc extracted using aqua regia increased with increase of the clay size proportion. Concerning potentially pollutant elements, As contents increase with decreasing particle size, and very high concentrations of Cr were found in some soils. However, As is less available in the finer soils and the percentages of extraction of Cr are low, limiting eventual environmental and health effects in the Santiago island.

1. Introduction

Environmental monitoring studies are essential for the establishment of guidelines for preservation of the environment and for the identification of potential focus of pollution/contamination of superficial topsoil layers. In issues related with geological problems, the chemical analyses of geologic materials are of great interest for the determination of natural background and further evaluation of geogenic sources or anthropogenic contributions for the chemical elements distribution in soils.

Geochemical mapping to produce multi-element data bases has been widely used and applied in diverse areas, such as environmental studies, agriculture, geomedicine and mineral explorations (Xuejing and Hangxin, 2001; Prohic et al., 1997; Ódor et al., 1997; Ferreira et al., 2001; Inácio et al., 2008). The use of soil or regolith samples for geochemical mapping in areas, where stream sediments do not occur is recommended by Darnley et al. (1995), but this has so far been limited to local geochemical surveys. A limited number of regional studies, such as geochemical mapping projects in China and in the North American Prairie have been based on soil samples (Prohic et al., 1997).

The geology, volcanology and hydrogeology of the Cape Verde archipelago, focusing on Santiago island, have been investigated by several studies (Matos Alves et al., 1979; Gomes and Pina, 2003; Pina et al., 2005; Monteiro Santos et al., 2006; Carreira et al., 2010; Martins et al., 2010). A low sampling-density survey of the geochemistry of rocks, soils, stream and sediments of Santiago island was done previously in the frame of a large project aiming to construct an environmental atlas of the island. Concerning soils, 249 samples (residual soils and upper horizon of sediments), taken in 2005/2006, at a density of 0.28 samples per km^2, were studied including the chemical (aqua regia extractable solution) and mineralogical characterization, as well as the grain-size distribution. The chemical analysis was performed using ICP-AES, after digestion in a modified aqua regia solution. The geochemical patterns obtained from spatial distribution maps were correlated with several factors such as the nature of the parent material, the soil type and some sources of anthropogenic contamination (Cabral Pinto, 2010; Hernandez, 2008).

The analysis of whole samples to evaluate total concentrations determines the true extent of chemical elements levels in soils. The present work aims to further develop the geochemical atlas

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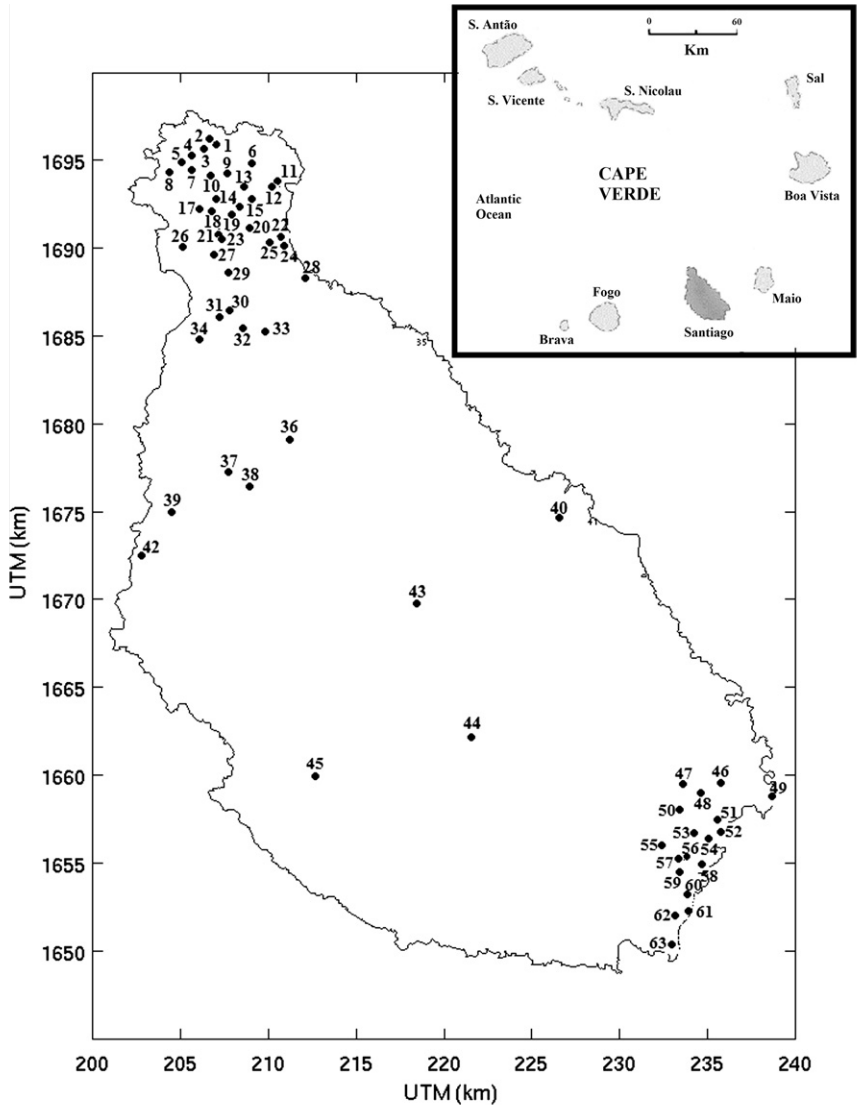

Fig. 1. Location of Santiago island in Cape Verde archipelago, and location of soils (coordinates are given in Table 2).

of Santiago for a wide range of major and trace element concentrations (Na, K, Fe, Sc, Cr, Mn, Co, Zn, Ga, As, Br, Rb, Zr, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th and U) in total soil samples using instrumental neutron activation analysis (INAA), to contribute to the understanding of the geochemistry of rare earth elements (REEs) and other trace elements in volcanic soils. The total contents in 63 soils developed in different geological formations were compared with the aqua regia extractable fractions, and grain size distributions, and the availability of chemical elements in this type of soils may be evaluated. It aims to use these analyses to identify factors controlling the total and bioaccessible concentrations of chemical elements in the soils of Santiago. This is crucial information for environmental studies (Amaral et al., 2006; Alloway, 1995), and is particularly important when dealing with volcanic regions, where some magmatic processes may produce an imbalance of elements in volcanic parent materials that can impact on the health of plants and animals growing in or on the soils developed on them (Neall, 2007).

The main objectives of this work are therefore: (1) the chemical characterization (total contents) of the whole sample ($\varnothing < 2$ mm) of the topsoil layer of 63 Santiago soils developed on all geological formations of the island (volcanic rocks and Quaternary sedimentary deposits), contributing for the establishment of the geochemical baselines; (2) the establishment of types of soils based on geochemical patterns or chemical tracers; (3) the correlation between total contents of chemical elements and the grain size distribution, particularly the $\varnothing < 2$ μm fraction proportion; and (4) the evaluation of the extractable fraction of selected elements by aqua regia digestion and its correlation with the grain size.

2. Geological setting, climate and study area

The Cape Verde archipelago consists of nine inhabited islands, one uninhabited island and various islets, located between 14°30′ and 17°30′N and between 22°30′ and 25°30′W (Atlantic Ocean, 500–800 km westwards of Africa) (Fig. 1). This archipelago belongs to the Macaronesia region along with Madeira, the Azores, Canarias and Savage islands.

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), a belt of converging trade winds

Table 1
Radionuclides, cooling times, energies of γ rays, and type of detector used.

Element	Radionuclide	Decay time (d)	Energy of γ-rays used (keV)	Detector coaxial Ge(Li)	LEPD
Na	^{24}Na	3	1368	x	
K	^{42}K	3	1524	x	
Fe	^{59}Fe	27	192; 1099	x	x
Sc	^{46}Sc	27	889	x	
Cr	^{51}Cr	27	319	x	x
Mn	^{56}Mn	0.11	846	x	
Co	^{60}Co	27	1332	x	
Zn	^{65}Zn	27	1115	x	
Ga	^{72}Ga	3	834	x	
As	^{76}As	3	559	x	
Br	^{82}Br	3	776	x	
Rb	^{86}Rb	27	1077	x	
Zr	^{95}Zr	27	756	x	
Cs	^{134}Cs	27	796	x	
Ba	^{131}Ba	27	496	x	x
La	^{140}La	3	1596	x	
Ce	^{141}Ce	27	145	x	x
Nd	^{147}Nd	27	91; 531	x	x
Sm	^{153}Sm	3	103	x	x
Eu	^{152}Eu	27	1408	x	x
Tb	^{160}Tb	27	879; 1178	x	x
Dy	^{165}Dy	0.10	95		x
Yb	^{169}Yb	27	177; 198	x	x
Lu	^{177}Lu	27	208	x	x
Hf	^{181}Hf	27	482	x	
Ta	^{182}Ta	27	1222	x	x
Th	^{233}Th	27	300; 312	x	x
U	^{239}Np	3	106; 228; 278	x	x

and rising air that encircles Earth near the Equator. 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, which when it does occur is often in the form of torrential downpours. These cause significant flooding and soil erosion. The few permanent watercourses in the islands are supplied by groundwater flow following such seasonal rains. In dry periods significant soil loss also occurs through deflation.

Santiago is the major island of the Cape Verde archipelago, with a surface area of 991 km^2 and a maximum elevation of 1394 m at Pico da Antónia. The terrain of this island varies significantly. The geology of Santiago island is mainly characterized by alkali basaltic rocks and respective pyroclastic products. Quaternary sediments and calcareous sedimentary rocks also occur, especially near Praia, São Francisco and Tarrafal bays. The main geologic units, from the newer to older ones are: sedimentary Quaternary formations (SED), the Monte das Vacas formation (MV), the Assomada formation (ASS), the eruptive complex of Pico da Antónia (PA), the Orgãos formation (FO), the Flamengos formation (FLA) and the Ancient Internal Eruptive Complex (CA).

3. Materials and methods

In the present work the total contents of 28 chemical elements of the whole sample (ø < 2 mm) of 63 soils from all geological units of the Santiago island, were obtained by INAA in the frame of the same project aiming the geochemical atlas of Cape Verde islands. The samples were aliquots of the same soil samples studied by Cabral Pinto (2010) and Hernandez (2008), which included both soils developed on volcanic rocks and Quaternary sedimentary deposits.

Two reference materials were used in the evaluation of elemental concentrations by INAA: soils GSS-4 and 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.

Irradiations were performed in the core grid of the Portuguese Research Reactor (Sacavém) at a thermal flux of 3.34×10^{12} n cm^{-2} s^{-1}; $\phi_{\mathrm{epi}}/\phi_{\mathrm{th}} = 1.4\%$; $\phi_{\mathrm{th}}/\phi_{\mathrm{fast}} = 12.1$. Two γ-ray spectrometers were used: (1) one consisting of a 150 cm^3 coaxial Ge detector connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. This system had a FWHM of 1.9 keV at 1.33 MeV; and (2) the other consisting of a low energy photon detector (LEPD) connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. This system had a FWHM of 300 eV at 5.9 keV and of 550 eV at 122 keV. 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). Details of the analytical method may be found in Prudêncio et al. (1986), Gouveia et al. (1992) and Prudêncio (2008).

Different cooling times were selected to determine radionuclides with different half-lives. These cooling times and energies of γ rays, as well as the type of detector used are given in Table 1. The chemical contents of Na, K, Fe, Sc, Cr, Mn, Co, Zn, Ga, As, Br, Rb, Zr, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th and U were obtained. Relative precision and accuracy are, in general, to within 5%, and occasionally within 10%.

Multivariate statistical methods were employed using the Statistica program (StatSoft, 2008). Hierarchical and non-hierarchical clustering methods: joining-tree and *K*-means, were applied. Concerning joining-tree clustering, the Ward's amalgamation method was employed. The Euclidean mean was used as the similarity coefficient to identify outliers and the Pearson correlation coefficient to evaluate correlation between variables. The goal of the *K*-means clustering procedure was to classify cases into a specified number of clusters (*K*), comparing the within cluster variability to the between cluster variability.

Table 2
Chemical results obtained by INAA of the whole sample (<2 mm) of topsoils of the Santiago island. Major elements are expressed in% oxide and trace elements in μg/g.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Field reference	7.49 PF	SO 7.49	296.49	5C.48	5B.48	293.49	1.48	5.48	283.49	281A.49	6.49	5.49	289.49	280B.49
X	206,517	206,514	206,072	205,386	204,949	208,937	205,524	204,144	207,540	206,435	210,165	209,952	208,212	206,628
Y	1,696,030	1,695,962	1,695,853	1,695,306	1,695,025	1,694,933	1,694,570	1,694,475	1,694,236	1,694,209	1,693,727	1,693,719	1,693,539	1,693,031
Geol. formation	PA	PA	PA	PA	PA	MV	FO	SED	PA	MV	PA	PA	CA	PA
Chemical group	II	II	III	II	II	II	III	I	III	II	Outlier	II	III	III
Na_2O	1.04	1.01	0.567	0.741	0.992	0.408	1.02	2.98	0.97	0.578	2.12	0.507	1.28	0.908
K_2O	1.57	1.62	1.38	1.62	1.73	1.76	1.37	4.42	1.77	1.09	3.29	1.57	2.62	1.29
Fe_2O_3T	15	12.4	17.1	12.9	14	12.8	14.6	6.63	14.3	13.9	10.4	14	11.2	15
Sc	24.7	20.7	30.7	24.6	26	23.9	26.5	9.61	24	29	21.4	27.4	19.9	28.7
Cr	631	593	680	650	735	628	562	113	873	765	149	669	371	698
Mn	1772	1726	1842	1842	2129	1587	1803	1765	2074	1649	2949	1672	1927	1718
Co	64.8	53.5	74.3	61	76.4	55.8	62.8	16.4	71.4	62	36.2	61.9	45.6	61.6
Zn	183	157	197	137	142	127	202	157	170	182	244	124	175	194
Ga	44.5	26.1	33.3	25.8	33.7	24.9	30.5	41.9	27.2	20.6	31	26.9	38.3	26.1
As	3.34	4.54	2.89	4.37	4.03	3.23	2.74	3.59	4.55	1.94	4.67	4.06	4.8	5.85
Br	16.7	17.2	11.8	23	19.7	14.9	22.7	9.22	15.8	16.5	7.95	23.4	16	16.5
Rb	35.5	35.2	54.5	53	53.9	67.4	53.9	167	51.9	66.6	100	82.9	72.6	39
Zr	397	369	382	272	351	371	534	719	350	382	591	254	580	496
Cs	1.77	2.19	1.66	2.07	1.99	2.34	1.34	3.08	2.28	1.35	2.34	2.13	2.33	1.19
Ba	719	651	688	552	697	604	645	368	622	609	2460	530	1097	514
La	61.5	52.9	80.2	51.6	61.3	59.7	88.6	118	63.8	64.1	413	61.3	99.2	93
Ce	141	121	167	123	154	132	194	297	182	137	685	130	218	180
Nd	59.6	51.7	77.3	46.4	57.8	57.9	96.3	82.6	58.8	64.8	210.7	60.0	89.0	92.1
Sm	10.4	8.85	12.9	8.55	9.82	9.94	16	10.8	10.9	10.7	24.5	11	15.1	15.8
Eu	3.23	2.65	4.14	2.19	2.69	2.97	4.97	2.9	3.11	3.38	7.47	2.86	4.34	4.63
Tb	1.31	1.18	0.999	0.919	1.08	1.45	1.74	1.39	1.3	1.25	1.92	1.15	1.79	1.65
Dy	5.85	6.05	8.08	5.94	6.12	6.94	8.9	5.85	7.32	7.37	12.9	7.17	8.59	8.41
Yb	3.12	3.1	3.39	2.62	2.99	3.14	3.71	5.29	3.54	2.67	6.81	3.06	4.73	3.54
Lu	0.377	0.393	0.323	0.387	0.403	0.413	0.433	0.612	0.418	0.432	0.86	0.451	0.506	0.34
Hf	8.59	8.29	9.2	8.2	8.59	8.45	11.1	15.8	10.3	7.33	9.65	8.53	13	11.4
Ta	5.66	5.35	6.48	4.96	5.95	5.45	7.27	11.9	7.47	5.35	4.45	5.66	8.33	6.52
Th	8.98	9.9	9.03	8.96	9.96	9.39	9.06	16.5	11.4	7.22	36.7	9.24	13.1	9.17
U	2.13	2.48	1.84	1.82	2.96	1.38	1.6	1.97	3.38	n.d.	6.06	2.33	4.89	2.42

Sample	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Field reference	10.49	294.49	3.48	280.49	294A.49	282.49	4.49	297A.49	9.49	284.49	291.49	2.48	3.49	291A.49
X	208,673	207,971	205,733	206,395	207,518	208,609	207,039	210,362	206,980	209,904	209,904	204,817	206,570	211,959
Y	1,692,819	1,692,452	1,692,275	1,692,217	1,692,000	1,691,200	1,690,992	1,690,696	1,690,562	1,690,429	1,690,429	1,690,162	1,689,738	1,688,678
Geol. formation	PA	CA	PA	SED	MV	PA	PA	MV	PA	PA	PA	SED	PA	PA
Chemical group	III	I	III	II	III	III	II	II	II	II	II	II	II	III
Na_2O	1.05	2.27	1.79	0.371	0.573	0.543	1.22	0.603	1.26	1.39	0.621	1.58	1.3	0.599
K_2O	2.17	3.4	2.75	1.24	2.01	1.51	1.61	1.34	1.81	1.8	1.55	1.65	1.7	1.44
Fe_2O_3T	12	6.95	13.3	11.3	12.7	15.3	14.2	15.1	15.5	13.1	14.2	13.2	15	15.7
Sc	20.3	9.15	20.5	21.9	21.3	23.3	19.4	28.8	20	21.7	25.3	17.7	15.7	31.7
Cr	782	96.5	509	369	243	974	241	778	101	875	1570	162	130	717
Mn	2051	1811	3127	2059	1687	2012	1950	1711	1842	1734	1958	1726	2175	1316
Co	71.4	18.7	54	46.7	52.3	60.1	39.6	72	37.5	49.8	74.4	31.8	29.5	59.8
Zn	127	104	205	126	115	171	163	173	155	167	143	194	141	158
Ga	22.4	26.4	24.8	23.8	25.8	21.8	20.5	27.6	28.3	46.2	20.4	17.5	27.3	33.1
As	3.4	3.54	5.12	8.87	6.01	3.78	2.16	1.88	2.6	1.88	4.34	1.53	2.4	5.36
Br	13.8	10.5	8.87	15.7	27.1	13.7	12.6	19.4	17.3	17.3	12.5	13	27.5	30.3
Rb	66.8	93.1	92.7	54.2	72.2	65	59.6	58	47.5	73.5	64.8	72.5	61.8	53.3
Zr	396	445	474	299	409	363	366	371	320	374	432	287	354	431
Cs	1.87	1.85	2.92	1.42	2.63	1.89	1.57	1.08	1.85	2.06	2.22	1.57	1.81	2.82
Ba	803	1302	762	317	675	436	722	598	751	798	607	662	838	695
La	74.6	75.5	89	65.2	65.4	67.6	57.2	53.6	47.7	50.7	49.4	50.8	57.6	65.9

(*continued on next page*)

Table 2 (*continued*)

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ce	173	168	195	126	158	155	127	110	110	103	129	110	138	127
Nd	71.9	61.0	79.2	59.8	65.7	70.2	67.5	51.3	50.8	43.5	49.3	59.1	64.4	65.4
Sm	12.1	10.2	12.9	10.8	11.5	12.5	11.9	9.99	9.72	7.98	8.98	10.7	11.6	12.3
Eu	3.31	2.83	3.92	2.92	2.84	3.78	3.62	3	3.09	2.38	2.64	3.39	3.42	3.56
Tb	1.28	1.1	1.38	1.31	1.2	1.38	1.1	1.11	1.3	1.72	1.18	1.24	1.14	2.13
Dy	7.5	6.49	7.17	6.27	8.23	7.65	7.26	6.19	5.41	4.45	5.98	6.3	7.04	8
Yb	3.5	3.41	4.21	2.59	3.59	3.62	2.83	2.18	2.68	2.24	3.31	2.99	3.05	3.41
Lu	0.366	0.411	0.487	0.327	0.523	0.124	0.466	0.349	0.341	0.503	0.409	0.372	0.33	0.371
Hf	9.85	9.51	10.9	6.44	9.52	9.6	7.93	7.16	7.16	7.94	9.68	6.97	8.21	9.04
Ta	6.69	7.72	7.81	4.25	6.14	6.7	5.7	5.27	5.25	7.1	6.67	5.16	6.33	5.81
Th	9.67	10	11.3	7.11	10.8	9.78	6.34	6.4	7.21	7.8	10.4	6.32	7.4	9.47
U	1.83	2.19	2.03	1.39	2.43	2.22	1.1	1.51	1.52	2.4	2.21	1.25	1.37	2.44
Sample	29	30	31	32	33	34	35	36	37	38	39	40	41	42
Field reference	2.49	5A.51	5.51	4.51	6.51	7.51	13.51	1.51	2.51	3.51	262A.50	268.52	268A.52	249A.53
X	207,498	207,370	206,842	208,199	209,507	205,692	218,411	210,765	207,354	208,633	204,126	226,219	228,131	202,484
Y	1,688,662	1,686,478	1,686,230	1,685,581	1,685,285	1,684,882	1,684,731	1,679,190	1,677,313	1,676,555	1,675,183	1,674,694	1,674,515	1,672,551
Geol. formation	PA	PA	PA	PA	SED	SED	PA	PA	ASS	MV	ASS	PA	SED	PA
Chemical group	II	III	II	III	III	II	III	II	III	II	III	II	II	II
Na$_2$O	0.674	1.41	1.01	0.221	0.563	1.58	0.624	0.535	0.246	1.05	0.843	0.984	1.12	0.799
K$_2$O	1.05	1.18	0.854	0.449	0.859	1.14	1.34	0.729	1.21	1.06	1.37	0.902	1.06	1.54
Fe$_2$O$_3$T	15	15.6	10.6	17.4	15.9	15.3	16.3	13.9	19.3	17.7	18.5	15.8	12.8	15
Sc	29.3	18.9	17.1	21.4	29.1	27.3	27.5	27.1	23.2	23.1	23.4	29.5	30.8	23.4
Cr	590	136	337	152	593	512	612	517	135	85.5	52.4	568	501	382
Mn	1803	1935	1695	2229	2167	1633	2136	1656	1865	1772	2198	1556	1440	2028
Co	67.5	43.1	41.6	50.8	72.6	61.8	81.3	59.6	50.6	44.7	42.6	70.9	53.1	54.2
Zn	159	161	122	158	191	149	167	140	138	152	157	153	161	203
Ga	21.3	32.7	25.6	29.6	33	24.6	28.9	30	32	33.4	37.6	35.3	18.4	25.4
As	n.d.	2.37	0.905	1.69	3.32	n.d.	5.07	1.06	4.53	2.2	2.56	2.54	n.d.	2.99
Br	18.7	13.8	8.74	13.9	13.8	6.53	16.3	3.67	23.1	18.3	27.2	13.3	74.9	13
Rb	38	50.7	42.3	30.8	75.2	49.3	48.9	43.7	147	85	79.7	38.2	50.8	97.2
Zr	371	464	398	419	403	332	443	401	401	367	354	355	381	292
Cs	1.59	1.81	1.26	1.43	2.19	0.809	2.56	0.71	2.94	1.73	2.07	1.41	0.921	1.65
Ba	641	989	1009	839	716	757	607	769	650	937	851	540	482	602
La	59.4	75.5	83.5	92.8	69.5	58.3	60.2	98.4	82.1	61.8	72.1	46.1	58.4	58.5
Ce	128	172	177	204	162	116	145	175	165	154	164	99.7	114	134
Nd	59.5	84.5	77.5	102	64.3	60.4	65.0	80.7	84.0	61.1	70.0	50.6	55.7	58.6
Sm	10.7	13.4	12.1	16.8	11.3	10.3	11.4	12.8	14.4	11.2	12.7	9.28	9.69	10.8
Eu	3.39	4.14	3.56	5.29	3.62	3.37	3.59	3.9	4.01	3.41	3.85	3.13	3.26	3.41
Tb	1.21	1.62	1.03	1.92	1.42	1.5	1.64	1.59	1.35	1.23	1.28	1.41	1.19	1.4
Dy	6.76	8.26	7.09	10	7.64	6.46	7.92	6.64	8.57	6.92	8.61	6.14	6.2	6.55
Yb	2.68	3.61	3.27	4.31	3.28	2.74	3.87	2.93	3.76	2.78	3.24	2.71	2.37	3.26
Lu	0.267	0.423	0.375	0.459	0.376	0.337	0.521	0.346	0.497	0.466	0.322	0.327	0.272	0.389
Hf	8.37	9.63	8.71	10.3	8.82	7.99	9.92	8.38	9.19	8.03	8.52	7.45	7.21	8.05
Ta	6.36	9.83	8.62	9.05	6.27	6.45	5.97	6.96	6.75	6.41	6.94	4.66	5.41	5.94
Th	7.61	7.8	8.07	9.01	9.7	6.08	10.1	11.3	10	6.62	7.48	6.28	6.18	8.27
U	1.5	1.44	1.48	1.46	1.97	0.805	2.12	2.31	2.18	1.27	1.2	1.07	1.19	1.52
Sample	43	44	45	46	47	48	49	50	51	52	53	54	55	56
Field reference	238A.54	109.55	22.57	M.59	W.59	L.59	R.59	K.59	Q.59	DA.59	J.59	F.59	I.59	P.59
X	218,079	221,255	212,399	235,372	233,141	234,259	238,320	232,969	235,203	235,280	233,834	234,798	232081	233406
Y	1,669,843	1,662,040	1,659,994	1,659,537	1,659,535	1,659,100	1,658,890	1,658,018	1,657,297	1,656,904	1,656,757	1,656,496	1655865	1655358
Geol. formation	FLA	MV	PA	CA	PA	CA	PA	CA	PA	FLA	SED	FLA	CA	FO
Chemical group	II	III	I	I	II	II	II	II	II	II	I	II	I	II
Na$_2$O	0.72	0.224	1.94	1.76	0.477	0.354	1.3	0.487	0.684	0.507	2.05	0.281	4.4	0.507
K$_2$O	1.11	0.234	2.97	3.83	1.09	0.364	1.2	1.23	0.927	0.767	3.34	0.391	3.54	1.19

Fe_2O_3T	15.6	17.1	7.04	7.27	17.8	12.6	13.6	12.7	12.3	14.2	8.43	16.7	6.08	16.1
Sc	28.3	30.5	8.08	6.62	36.5	24.9	42.2	29.8	24.5	35.8	15.7	38.9	6	30.9
Cr	493	641	103	97.7	743	900	497	576	417	1080	131	1410	93.1	643
Mn	1850	1989	1308	1997	1811	1571	1091	1161	1718	1633	1339	1339	1277	1819
Co	70.4	82.6	16.4	16.4	79.3	75.8	55.1	52	50.1	60	31.8	53.5	14.5	71
Zn	183	187	111	115	171	127	118	150	122	157	154	183	130	144
Ga	23.7	24.5	45.3	22.7	34.4	17.5	33	27.8	24.4	24.4	36.2	25.9	0.1	25.8
As	1.07	1.74	4.28	1.26	n.d.	1.18	7.04	1.21	n.d.	1.03	2.2	1.67	3.41	1.52
Br	4.52	31.2	27.4	5.45	20.2	9.71	39.9	20.4	3.39	10	36.3	7.43	8.1	15.6
Rb	53.5	n.d.	125	63	33.7	22.6	31.3	65.5	19.1	43.2	140	26.1	114	45.3
Zr	453	435	801	471	326	332	447	291	370	416	525	392	581	315
Cs	0.564	1.16	1.95	1.66	1.82	0.458	2.99	0.854	0.709	1.02	1.8	0.574	1.52	1.09
Ba	617	954	710	1881	467	745	268	393	687	580	1402	441	1027	548
La	72.7	90.5	116	103	53.1	71.4	68.4	56.3	60.7	51.5	89.4	59.2	104	48.3
Ce	143	161	252	192	120	139	127	106	119	101	164	120	199	108
Nd	69.3	75.3	53.3	72.0	54.9	69.3	67.7	55.0	60.0	51.4	58.1	60.5	74.7	55.4
Sm	11.4	12.9	7.48	11.2	10.1	11.4	11.6	10.7	9.04	9.97	10	11.6	10.9	9.8
Eu	3.73	4.2	2.37	3.29	3.37	3.29	3.63	3.21	3.08	3.2	3.15	3.75	3.71	2.93
Tb	1.41	1.6	1.08	1.21	0.989	0.935	1.24	1.58	1.03	1.3	1.13	1.32	1.01	1.27
Dy	6.73	7.52	5.56	6.44	6.66	6	7.3	6.66	6.31	6.24	6.56	6.78	6.24	6.31
Yb	3.01	2.74	3.74	3.4	2.93	1.82	2.8	2.48	2.36	2.38	3.28	2.43	4.36	2.39
Lu	0.279	0.3	0.295	0.382	0.382	0.21	0.387	0.416	0.265	0.748	0.302	0.365	0.421	0.322
Hf	7.86	7.13	17.3	10.1	7.96	5.38	7.87	7.61	7.62	8.21	12.2	9.45	13.1	6.86
Ta	6.48	5.98	9.28	7.28	6.02	4.36	4.63	5.66	5.61	5.31	8.27	6.14	13.2	5.44
Th	7.1	8.01	20.5	10.3	7.62	6.81	7.35	5.66	5.84	5.71	12.7	5.94	14	5.05
U	1.3	1.27	2.73	0.878	1.39	1.2	1.64	1.34	0.687	n.d.	4.08	1.03	4.41	1.2

Sample	57	58	59	60	61	62	63
Field reference	H.59	C.59	G.59	Z.59	O.59	B.59	A.59
X	233,220	234,314	233,120	233,578	233,559	232,909	232,652
Y	1,655,236	1,654,915	1,654,688	1,653,384	1,651,994	1,651,824	1,650,152
Geol. formation	CA	PA	CA	PA	PA	PA	PA
Chemical group	III	II	III	III	II	III	II
Na_2O	0.507	0.726	0.374	0.406	0.747	0.363	0.783
K_2O	1.86	0.654	1.48	1.52	0.79	1.45	1.24
Fe_2O_3T	16.2	14.9	15.9	17.6	13.7	21.1	17.6
Sc	33.8	43.7	31.1	26.5	31	35.6	30.4
Cr	677	1340	628	837	598	729	949
Mn	1726	1262	1672	2129	1548	1904	1881
Co	69.8	60.3	62.6	75	65.9	79.1	76.1
Zn	189	169	200	141	127	177	176
Ga	31.2	19.2	22.7	23.8	28.7	39.6	24
As	2.01	0.91	1.61	3.24	2.08	4.23	2.31
Br	12.8	5.3	11.8	13.6	16.9	15.7	13.6
Rb	73.6	26.5	36.8	46.4	26.2	60.3	39.1
Zr	423	322	484	331	354	498	236
Cs	1.13	n.d.	1.27	2.00	1.1	1.65	1.03
Ba	705	352	671	573	678	589	550
La	74.8	39.2	77.9	75.4	59.1	70.8	51.5
Ce	150	76	153	165	116	143	103
Nd	72.7	44.4	74.9	80.9	61.6	73.4	54.2
Sm	13.3	8.27	13.3	14.4	10.9	12.9	10.2
Eu	4.05	2.8	4.21	3.92	3.16	4.06	3.17
Tb	1.46	1.21	1.47	0.859	1.06	1.81	1.29
Dy	7.05	5.69	7.95	8.07	6.45	7.94	6.45
Yb	3.1	1.7	3.07	3.42	2.10	3.58	2.62
Lu	0.392	0.295	0.434	0.445	0.30	0.40	0.311
Hf	9.67	6.54	9.92	9.02	6.84	8.99	7.30
Ta	7.37	4.38	7.59	6.49	5.35	6.81	5.76
Th	8.18	4.32	7.97	8.85	5.43	8.17	5.75
U	2.43	1.38	1.99	1.92	0.841	1.64	n.d.

Table 3
Mean and variation coefficient (%), median, and minimum and maximum of total contents of the chemical elements obtained by INAA for 63 Santiago soils. Major elements are expressed in% of oxide and trace elements in µg/g.

	Mean	*c* (%)	Min	Max	Median
Na_2O	0.977	72.8	0.221	4.40	0.747
K_2O	1.571	54.4	0.234	4.42	1.380
Fe_2O_3T	14.1	21.9	6.08	21.1	14.3
Sc	25.0	31.0	6.00	43.7	24.9
Cr	546	61.7	52.4	1570	590
Mn	1806	19.2	1091	3127	1803
Co	55.8	31.3	14.5	82.6	59.8
Zn	158	17.8	104	244	157
Ga	28.4	23.6	17.5	46.2	26.7
As	3.12	53.1	0.905	8.87	2.82
Br	16.9	62.7	3.39	74.9	15.6
Rb	61.9	48.5	19.1	167	54.1
Zr	406	24.7	236	801	382
Cs	1.69	37.6	0.458	3.08	1.70
Ba	729	46.5	268	2460	671
La	74.7	62.5	39.2	413	65.2
Ce	156	49.7	75.9	685	143
Nd	68.0	32.7	43.5	211	64.3
Sm	11.5	21.9	7.48	24.5	11.0
Eu	3.50	22.4	2.19	7.47	3.38
Tb	1.33	20.0	0.859	2.13	1.29
Dy	7.05	17.6	4.45	12.9	6.76
Yb	3.17	25.4	1.70	6.81	3.10
Lu	0.39	28.2	0.12	0.86	0.38
Hf	8.98	22.8	5.38	17.3	8.53
Ta	6.51	25.1	4.25	13.2	6.27
Th	9.12	48.9	4.32	36.7	8.18
U	1.93	51.0	0.69	6.06	1.64

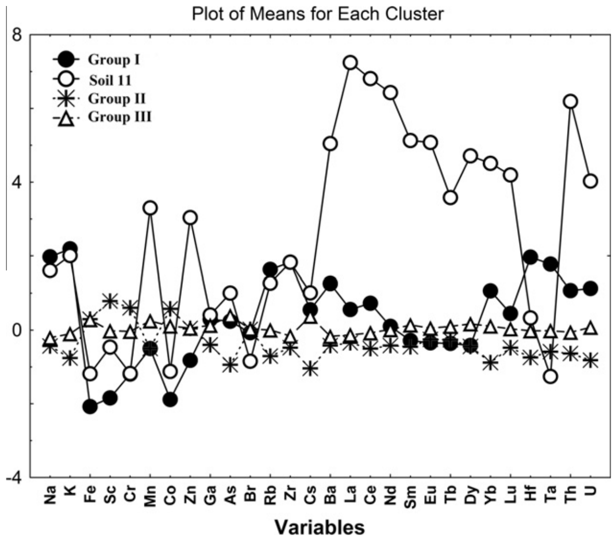

Fig. 2. Plot of means for all Santiago soils by means of clustering method (*K* = 4), using the total chemical contents as variables.

4. Results and discussion

The total contents of chemical elements obtained in this work by INAA for the 63 Santiago topsoils are given in Table 2. The sample reference, field reference, UTM coordinates and geological formation for each soil are also given. The mean values and corresponding variation coefficient (%), median, and minimum and maximum values are given in Table 3. A general significant variation of the total contents of the chemical elements studied was found, particularly for Na, K, Cr, As, Br, La, and U. The chemical results obtained in this work did not clearly differentiated soils developed in the different geological formations. Besides, despite the small number of samples for some geological formations, it was found that chemical contents of the elements studied may vary significantly within each geological formation. The largest variations were found in soils developed in Quaternary sediments, which can be explained by a variation in the source-area. A multivariate statistical study was then applied to establish types of soils based on the total contents of the chemical elements studied and cross information with the parent rock. A first approach by joining-tree clustering, using the Euclidean distance as the similarity coefficient and the Ward's amalgamation method, clearly showed the existence of one outlier (sample 11). This soil, collected near Tarrafal, north of Santiago (see Fig. 1), was also differentiated from the others by the *K*-means method (*K* = 4) (Fig. 2), mainly due to higher contents of Mn, Zn, and particularly Ba, REE, Th and U. The remaining samples were divided in three groups, and the allocation of the samples is indicated in Table 2 (chemical group). Group I formed by six soils, was clearly distinguished from the other groups, by lower contents of Fe, Sc, Cr, Co and Zn and higher contents of Na, K, Rb, Cs, and particularly Zr, Ba, light REE (LREE), heavy REE (HREE), Hf, Ta, Th and U. An important differentiation of group I was given by the proportion of middle REE (MREE) relative to the LREE and HREE. Groups II and III (containing 35 cases and 21 cases, respectively) include soils from several geological units – group II: 4 SED samples; 4 MV samples; 21 PA samples; 1 FO sample; 3 FLA samples; and 2 CA samples; group III: 1 SED sample; 4 MV samples; 2 ASS samples; 12 PA samples; 1 FO sample; and 1CA sample. These two groups are differentiated from each other mainly by Sc, Cr, As, Rb, Cs, HREE, Hf, Ta, Th and U.

The geochemical patterns of soil 11 and group I pointed to a carbonatite source (high contents of Ba, REE, Th and U). The chondrite-normalized REE patterns (values of Anders and Grevesse (1989) multiplied by 1.36, obtained by Korotev (1996a, 1996b) of these carbonatite-related soils are shown in Fig. 3a. Soil 11 has the higher REE contents, particularly the LREE and MREE. A significant variation of the REE pattern was observed for sample 8 (soil developed on Quaternary sedimentary deposits) and sample 45 (residual soil in PA formation), where a depletion of the MREE relative to the LREE and HREE occurs. A positive Ce anomaly is also observed in these two soils, suggesting oxidizing conditions that originate the preferential retention of Ce^{4+} (Dias et al., 2000; Gouveia et al., 1993; Prudêncio et al., 1995). In Fig. 3b the $(La/Sm)_{ch}$ vs. $(La/Yb)_{ch}$ clearly shows the differences found between samples from group I and sample 11 (closed circles), and soils belonging to groups II and III.

The correlation between the clay size proportion in soils and the chemical elements contents obtained by INAA can be used to illustrate the form/availability of the chemical elements in soils. The inclusion of clay size proportion as variable in joining-tree clustering shows its association with Cs, As and Ga (Fig. 4). Therefore a general increase of total contents of these elements with the increase of the clay size proportion appears to exist. Three other groups of elements are found in this phenogram and may be related with mineral phases: (i) the group of first-row transition elements, probably related with ferromagnesian minerals and/or hydrous oxides; (ii) the association of Na, K, Ba and Rb, elements usually related with the presence of feldspars (and barite); and (iii) the association of REE (particularly LREE and HREE) with actinides and Hf, Ta and Zr pointing to the presence of these elements in mineral phases like zirconolite, phosphates and carbonates. Manganese and bromine are not significantly correlated with other studied elements. Manganese may be related with the presence of brucite. Concerning

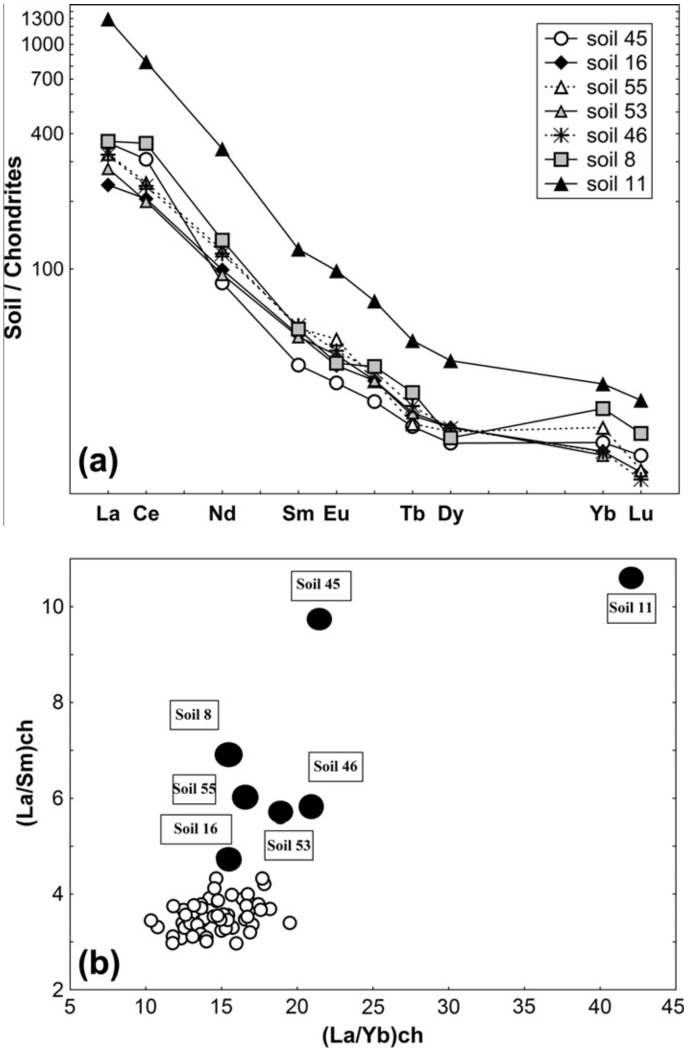

Fig. 3. (a) Chondrites-normalized REE patterns of soil 11 and other carbonatite related soils from Santiago island. (b) $(La/Yb)_{ch}$ vs $(La/Sm)_{ch}$ ratios of soils from Santiago island (soil 11 and group I are marked as close circles).

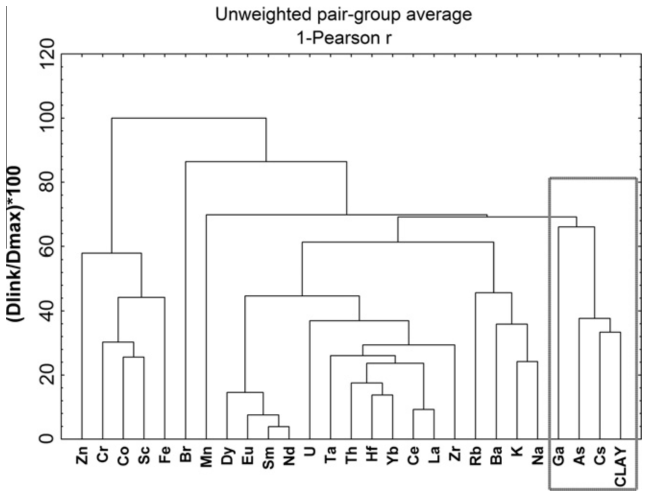

Fig. 4. Tree diagram resulting from the cluster analysis using the trace elements contents and the clay size proportion of Santiago soils as variables.

bromine, the variations of the total contents found may be largely controlled by the organic matter present in the soils, which has the ability to fix this volatile element added by wet deposition (ocean origin).

The evaluation of the availability of elements in soils, especially those potentially pollutants, is of great interest to environmental issues particularly related with health. A previous work, performed by Carreira et al. (2010), in order to understand the influence of the anthropogenic activities on the water quality and the main origin of the salts in groundwater in Santiago island, suggests that water–rock interaction is the major process responsible for producing the observed groundwater quality (mainly calcium-bicarbonate type), reflecting the lithological composition of the subsurface soil at Santiago island. In this report the total contents of Na, K, Fe, Sc, Cr, Mn, Co, Zn, Ga, As, Ba, La, Th and U in the studied Santiago soils, obtained in the present work, were compared with the respective concentrations in the aqua-regia extractable solutions, in order to estimate the percentages of elements extraction. A correlative study between total and percentage of extraction of each element, and the clay size proportion was also done. The biplot graphs of the clay size proportion *vs.* the total contents and the amount of extraction of each element are shown in Figs. 5–10. In these graphs, carbonatite-related soil

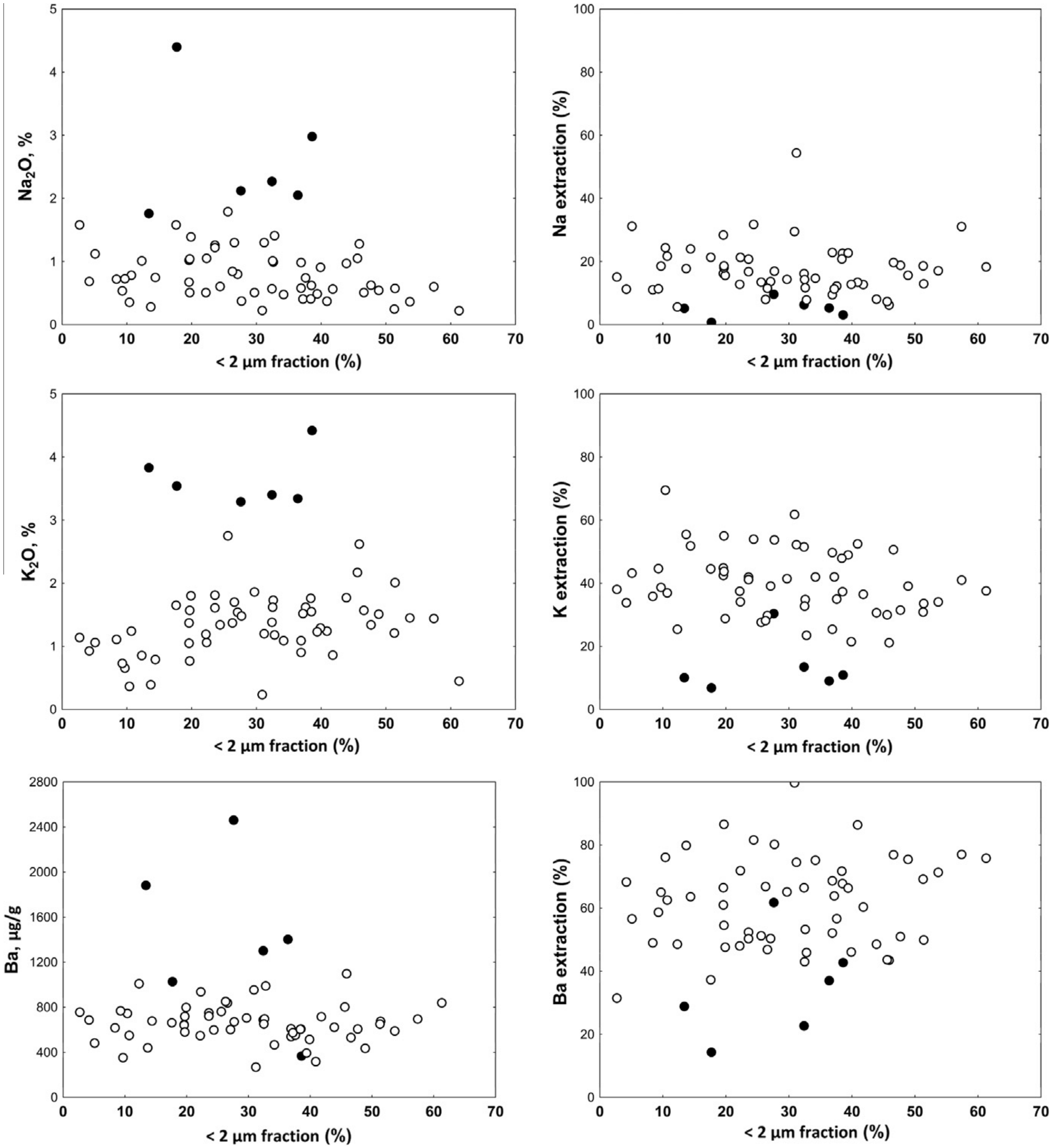

Fig. 5. Biplot graphs of the clay size proportion *vs.* total contents of Na, K and Ba, and aqua-regia extraction (%) of soils from Santiago island.

samples (sample 11 and group I defined above) are plotted with a different marker (closed circle). The results obtained showed a significant variation between the chemical elements contents and their availability in Santiago soils, and the grain size. Carbonatite-related soils presenting high total contents of Na, K and Ba, have low aqua-regia extraction (see Fig. 5), probably due to their presence mainly in feldspars and barite, minerals not so soluble in aqua-regia solution. Among these elements, Na is the less extractable in all studied soils. A wide range of aqua-regia extraction fraction was found for Ba (14–99%), pointing to its presence in different mineral phases such as feldspars and barite or in more soluble phases.

A significant variation of the total contents of Mn, Fe and Co in Santiago soils with a similar clay size fraction is observed, as shown in Fig. 6. However, positive correlations of the aqua-regia extractable portion of these elements with the clay size fraction

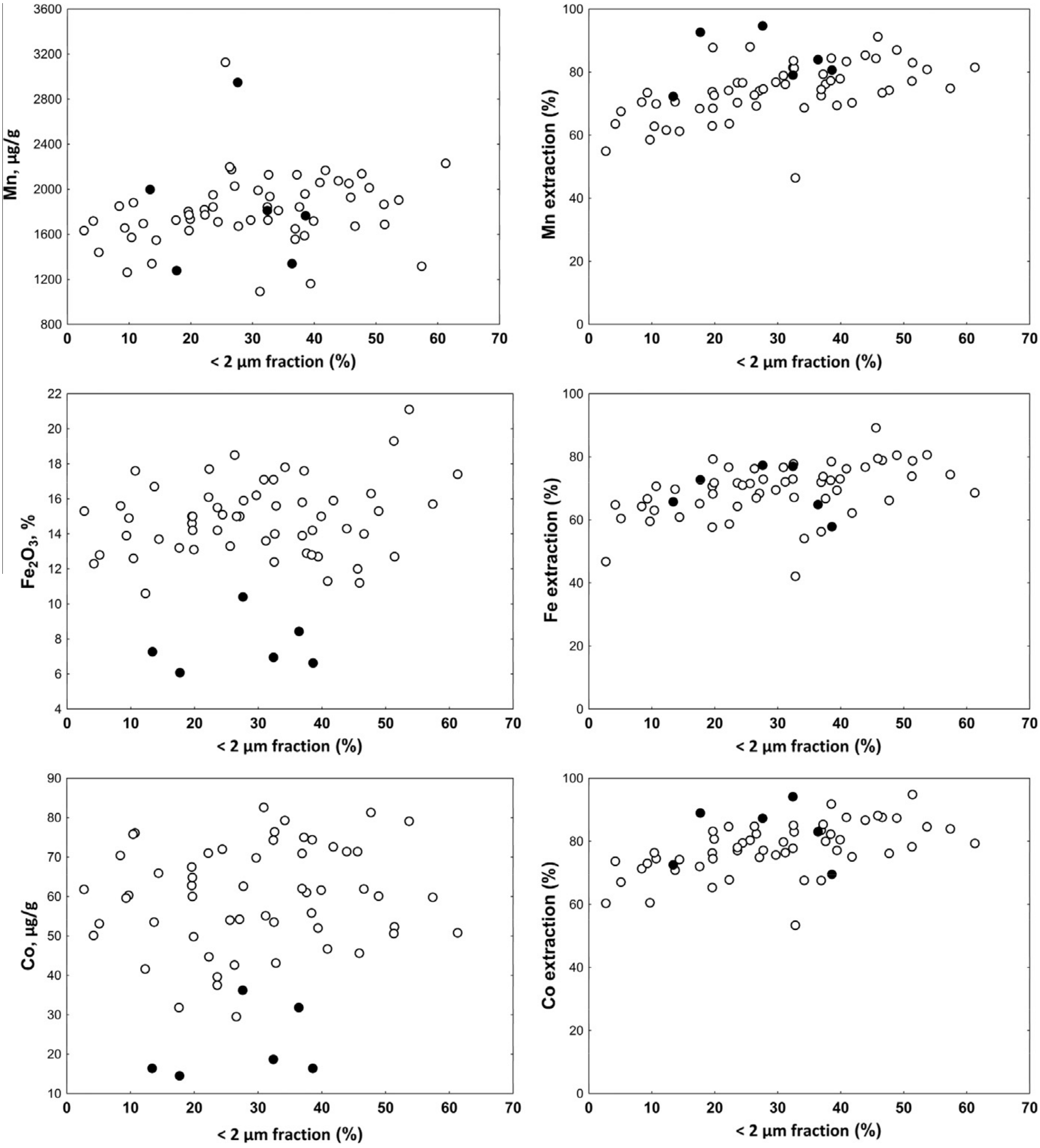

Fig. 6. Biplot graphs of the clay size proportion *vs* total contents of Mn, Fe and Co, and aqua-regia extraction (%) of soils from Santiago island.

proportion occur, pointing to the higher availability of these elements in soils with smaller particles. It should also be noted that, concerning Fe and Co, carbonatite-related soils have the lower total contents, but the values for extraction do not differ significantly from the other soils. This general tendency of availability (independent of the lithology) points to the presence of these elements in soluble phases, such as hydrous Fe/Mn oxides and/or carbonates (Prudêncio et al., 2010), or in the vitreous phase of these volcanic soils.

The amount of aqua-regia extractable fraction of La and Th in the studied Santiago soil samples do not depend significantly on the grain size (La ~ 65% and Th ~ 60%), as shown in Fig. 7, pointing to their presence mainly in more soluble forms (like phosphates or carbonates), independently of the grain size, even in the

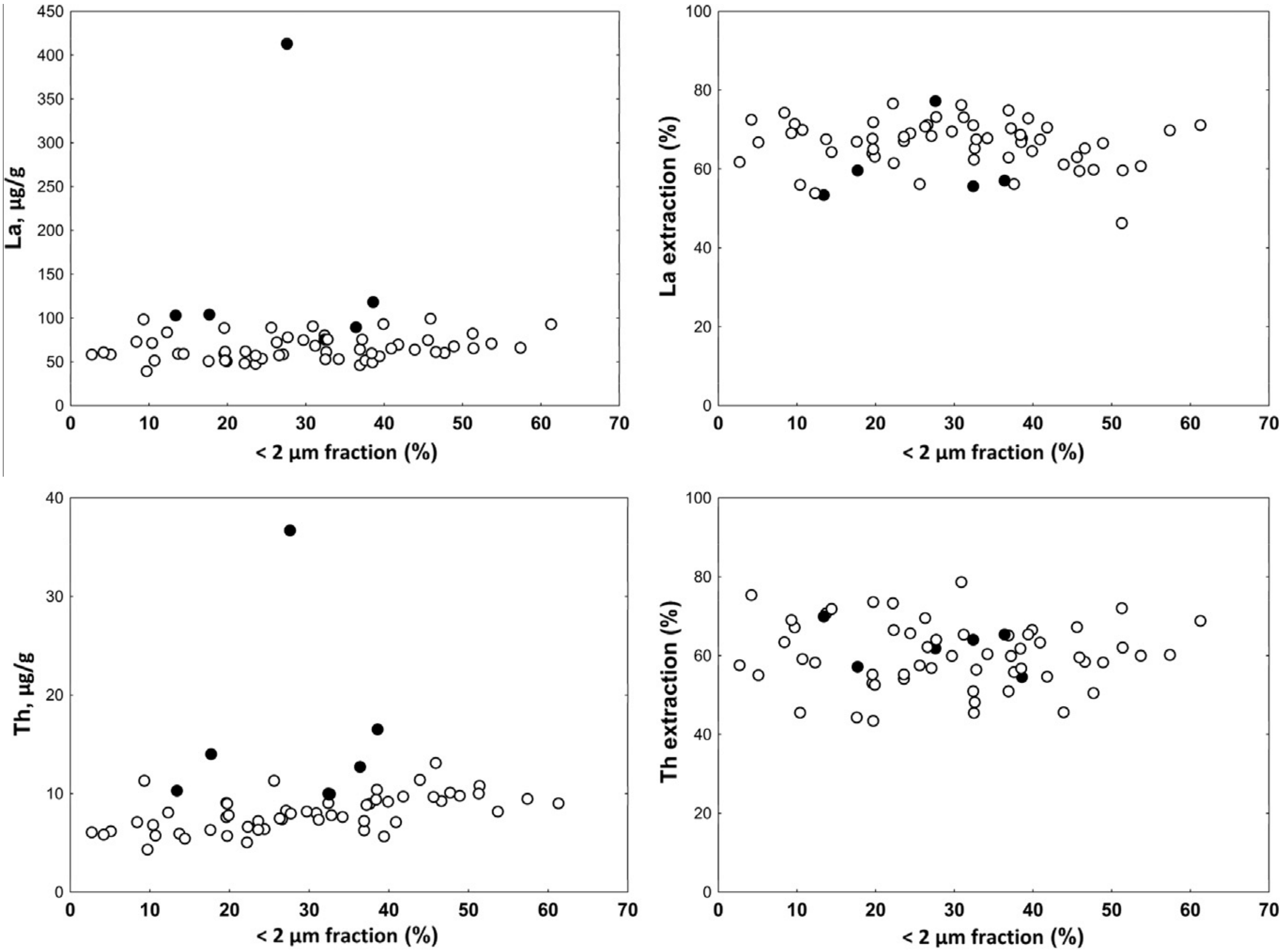

Fig. 7. Biplot graphs of the clay size proportion *vs* total contents of La and Th, and aqua-regia extraction (%) of soils from Santiago island.

carbonatite related soils, where the higher total contents of these elements were found.

The total contents of Sc do not depend on the clay fraction proportion (Fig. 8). Carbonatite-related soils have in general the lower Sc contents found in the studied soils. A similar distribution with the clay fraction was found for Fe and Co, as referred above, even for the extractable fraction, but with a lower degree of extraction. These results indicate the preferential presence of Sc in ferromagnesian minerals and/or phyllosilicates rather than in more soluble phases such as hydrous oxides or vitreous phase.

Concerning Ga, a tendency for an increase of the total contents with the decrease of particle size is observed (Fig. 8). No significant variations in the percentage of extraction of Ga with the clay proportion in the soil were observed, pointing to Ga distribution in particles of different size, probably replacing Al^{3+} in aluminium silicates (Prudêncio et al., 2010).

The total contents of Cr and Zn, two elements considered to be of great risk to environmental health (Kabata-Pendias, 2001), appear not depend on the clay size proportion of Santiago soils (Fig. 9). Carbonatite-related soils have in general lower contents than the other studied soils, particularly Cr. A tendency for an increase of the percentage of extraction of Cr seems to occur with the increase of the clay size fraction. Zinc extraction does not vary significantly with the clay size proportion; the higher percentages of extraction were found in carbonatite-related soils.

Concerning As and U, also two elements of potential health risk, although the total contents of these elements increase with the increase of the clay size fraction proportion, their availability for extraction with aqua-regia appears to be lower in the finer soils, particularly in case of As (Fig. 10). Thus, these elements may be present in different types of minerals according to the granulometry. The solubility, mobility and bioavailability of As are normally controlled by adsorption–desorption processes involving Fe, Al, Mn oxy-hydroxides, clay minerals, carbonates (under oxidizing conditions) and sulphide minerals (under reducing conditions) in normal soil conditions (Cullen and Reimer, 1989; Drahota et al., 2009). It should be noted that the variation of the percentage of As extraction with the clay size proportion in the studied samples soils is not correlated with the behaviour of Fe and Mn (see Fig. 6 and 8). Thus, As may occur mainly in mineral phases less soluble in aqua-regia solution such as phyllosilicates, particularly in the finer soils. Uranium also appears to be less available in the finer soils, but the correlation between clay size proportion and the percentage of extraction is not evident as the one found for As.

5. Conclusions

This paper presents the first results of total contents of trace and major elements in topsoils from Santiago island (Cape Verde),

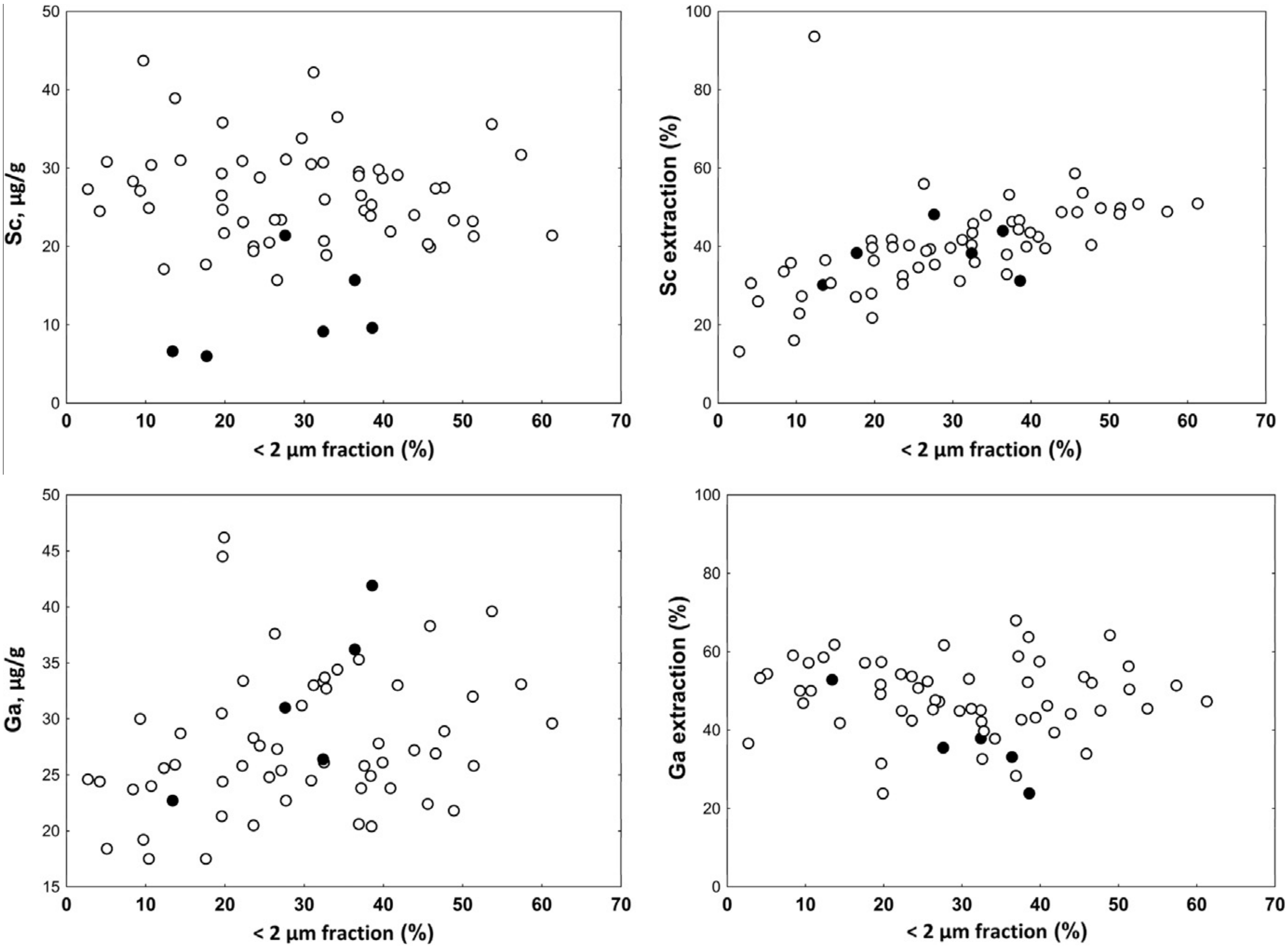

Fig. 8. Biplot graphs of the clay size proportion *vs* total contents of Sc and Ga, and aqua-regia extraction (%) of soils from Santiago island.

collected in 2005/2006 according to the recommendations of IGCP Project 259 "International geochemical mapping", contributing for the establishment of a low density geochemical atlas. Significant variations in the total contents were found: (i) >60% for Na, Cr, Br and La; (ii) 40–60% for K, As, Rb, Ba, Ce, Th and U; (iii) 20–40% for Fe, Sc, Co, Ga, Zr, Cs, Nd, Sm, Eu, Tb, Yb, Lu, Hf and Ta; and (iv) <20% for Mn, Zn and Dy.

No significant correlation was found between total contents of the studied elements and the geological formations. However, a multivariate statistical analysis using the total contents of chemical elements in Santiago soils developed on volcanic rocks and Quaternary sedimentary deposits from the several geological units of the island, could clearly distinguish soils with different contributions of carbonatite as parent material (residual and sedimentary deposits), mainly due to high contents of Ba, Th, U, and particularly REE. In fact, the results obtained so far indicated that REE may be used as a geochemical indicator to discriminate between contrasting parent materials, particularly the carbonatites-related soils from Santiago island. This type of soils have in general higher REE contents, higher $(La/Yb)_{ch}$, and particularly higher $(La/Sm)_{ch}$ ratios. This pattern can be inherited from the parent material or can be due to the preferential loss of MREE after breakdown of primary REE bearing mineral phases, followed by the preferential incorporation of LREE in Fe/Mn oxides and in clay minerals, and incorporation of HREE in secondary carbonates (calcite or dolomite) in the semi-arid climate of Cape Verde.

The clay size amount in soils is associated with total contents of Cs, As and Ga. The remaining elements studied group as follows: (i) first-row transition elements, (ii) Na, K, Ba and Rb, and (iii) REE (particularly LREE and HREE) with actinides and Hf, Ta and Zr; Mn and Br have singular behaviours.

An increase of the percentage of aqua-regia extraction of Fe, Co, Mn and Sc was found with the increase of the clay size proportion. The total contents of As (a potentially pollutant element) increases with decreasing of the particles size. However, it becomes less available in the finer soils, diminishing eventual environmental and health problems. The same tendency was observed for U. Concerning Zn and particularly Cr, elements considered to be of great risk to environmental health, are present in some of the studied soils in very high concentrations. However, the percentage of extraction of these elements is not very high (mean values of ~30% and ~50% for Cr and Zn, respectively).

The results obtained contribute to the geochemical characterization of superficial environments of the Santiago island, and the evaluation of availability of elements in the topsoil layer. A more complete study of the total contents in a larger number of soils developed in the different geological formations of the island is foreseen.

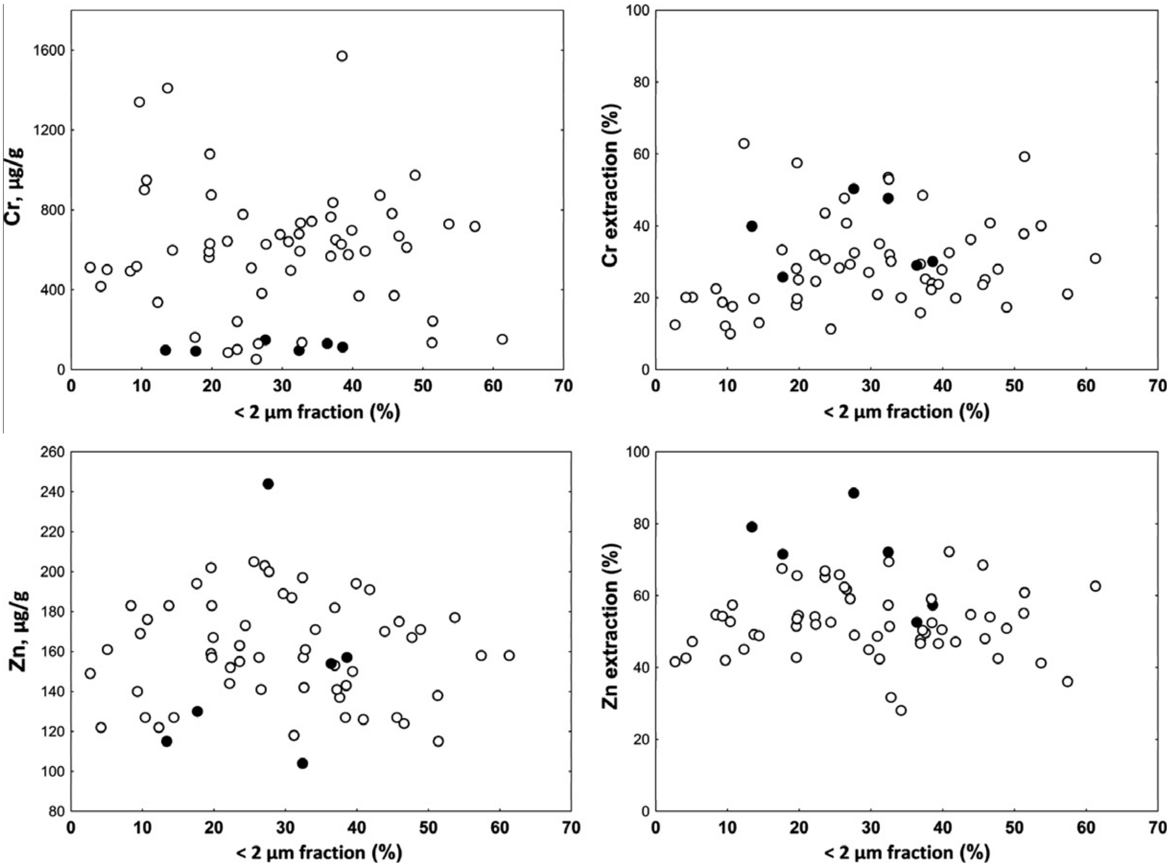

Fig. 9. Biplot graphs of the clay size proportion *vs* total contents of Cr and Zn, and aqua-regia extraction (%) of soils from Santiago island.

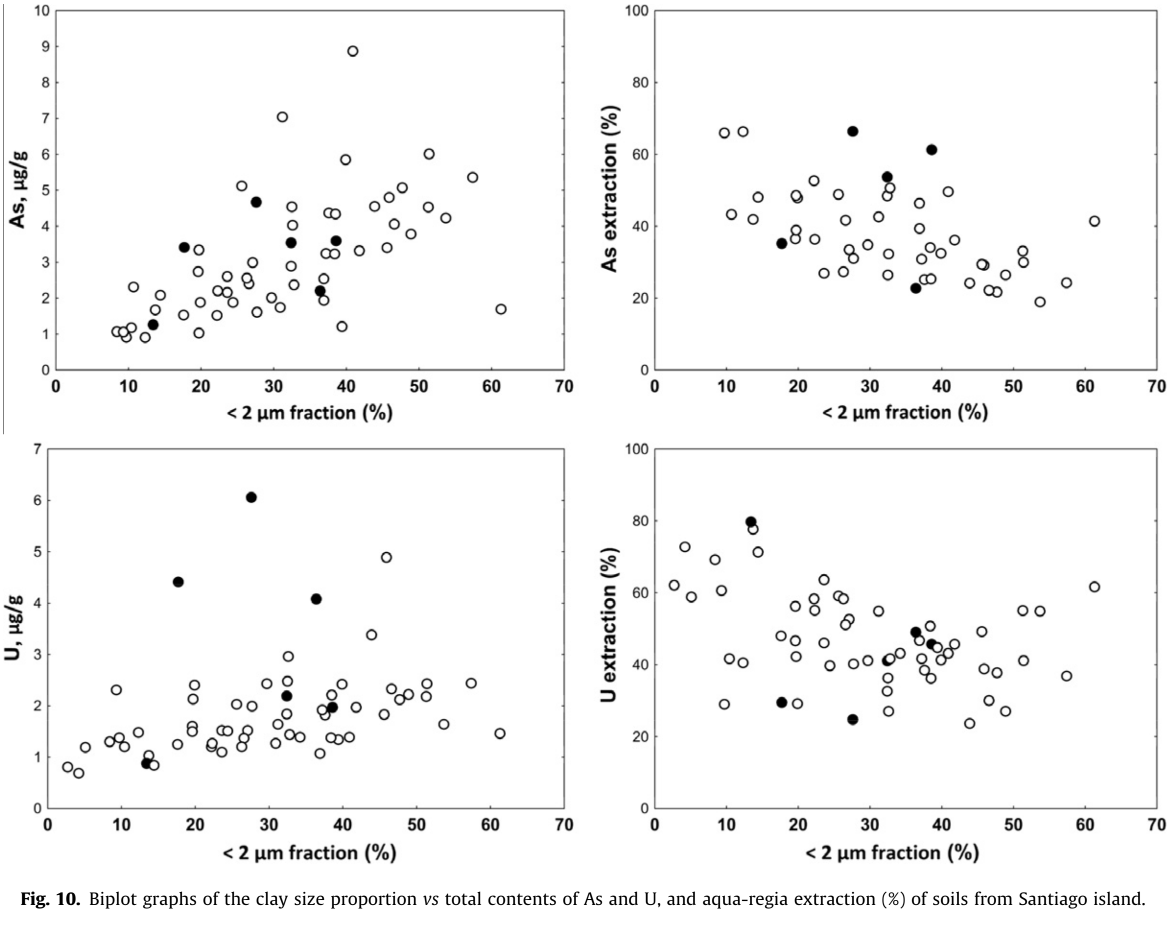

Fig. 10. Biplot graphs of the clay size proportion *vs* total contents of As and U, and aqua-regia extraction (%) of soils from Santiago island.

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