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SOIL GEOCHEMISTRY ADJACENT TO CARBONATITES FROM CAÇAPAVA DO SUL, RS, BY FLUORESCENCE OF X-RAYS BY DISPERSIVE ENERGY

GEOQUÍMICA DE SOLO ADJACENTE A CARBONATITOS DE CAÇAPAVA DO SUL, RS, POR FLUORESCÊNCIA DE RAIOS-X COM ENERGIA DISPERSIVA

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ABSTRACT - Currently, carbonatites are being severally studied in a prospective matter due to their high chance of containing calcium carbonate, magnesium and iron. They are also considered extremely rich in phosphate and minerals rich in Rare Earth Elements (ETR). In this context, the municipality of Caçapava do Sul has two occurrences of carbonatites: Picada de Tocos and Passo Feio. In order to enrich knowledge and assist in carbonate prospecting, this work aimed to characterize the soil geochemistry at the occurrences of the carbonatites in Caçapava do Sul. The data obtained revealed that there is an anomalous presence of Ca, Mg, Fe, Ti, P, Mn, Co, Th and Ce elements. This anomaly is directly linked to the presence of carbonatites in the region and their chemical composition.
Keywords: Carbonatite. PCA. Soil.

RESUMO - Atualmente, as carbonatitos estão sendo severamente estudados de maneira diversa em uma questão prospectiva devido à sua alta chance de conter carbonato de cálcio, magnésio e ferro. Eles também são considerados extremamente ricos em fosfato e minerais ricos em elementos de terras raras (ETR). Nesse contexto, o município de Caçapava do Sul possui duas ocorrências de carbonatitos: Picada de Tocos e Passo Feio. Com o objetivo de enriquecer o conhecimento e auxiliar na prospecção de carbonatos, este trabalho teve como objetivo caracterizar a geoquímica do solo nas ocorrências dos carbonatitos em Caçapava do Sul. Os dados obtidos revelaram a presença anômala de elementos Ca, Mg, Fe, Ti, P, Mn, Co, Th e Ce. Essa anomalia está diretamente ligada à presença de carbonatitos na região e sua composição química.
Palavras-Chave: Carbonatito. PCA. Solo.

INTRODUCTION

Actually, mining is present in several Brazilian sectors, including phosphate fertilizers. The growing demand for fertilizers in the current scenario of encouraging cultivation is great and, consequently, the demand for phosphorus-rich mineral deposits is also high. In this sense, carbonatites have significant advantages, as they contain high levels of phosphorus present in apatite, in addition to potassium (biotite and phlogopite), calcium (calcite), magnesium (dolomite) and rare metals (Mariano, 1989).

Carbonatites are unusual igneous rocks composed of more than 50% of primary carbonate, named after the main carbonated mineral that constitutes them, being thus divided into: calcitic, dolomitic, ferrocarbonatites and natrocarbonatites (Le Maitre, 2002; Mitchell, 2005; Jones et al., 2013). This type of rock is recognized on several continents, since the Precambrian (Tichomirowa et al., 2006; 2013; Woolley & Bailey, 2012). In Rio Grande do Sul four intrusions of carbonatite bodies are described: Picada dos Tocos and Passo Feio (identified by Mining Ventures Brasil; Rocha et al., 2013), in the region of Caçapava do Sul (targets of this work), Três Estradas (identified by Águia Metais; CPRM, 2010) in Lavras do Sul and Joca Tavares (CPRM, 2010) in Bagé.

In this sense, the study directed to geochemistry covers the distribution and migration of the chemical elements that constitute a given environment. The abundance of chemical elements both in primary environments (rock) and in secondary environments (soil, sediment and water) is intrinsically related (Dehbandi & Aftabi, 2016;

Campodonico et al., 2019). The chemical mobility between the atmosphere and the lithosphere, which modifies, transports and reallocates the chemical elements in response to the various processes that exist in this path (Meybeck & Helmer, 1992; Sahoo et al., 2017; Bessa et al., 2018).

The geochemical affinity of the elements is one of the principles that underlie the geochemistry applied to mineral exploration, since elements that belong to the same class can form geochemical associations indicative of certain mineralizations (Santos, 2014). On the other hand, elements of similar geochemical affinities may show different chemical mobility according to environmental conditions. Thus, those with greater mobility in the surface environment are used in prospecting as sniffing elements of those less mobile.

In the southern region of the state of Rio Grande do Sul, at least four occurrences of carbonatitic rocks have been reported in the literature. However, geochemical studies on the soils adjacent to these rocks have not yet been reported. In this study we seek to discuss the geochemical affinities recorded in these soils and their correlation with the carbonatitic rocks found locally.

LOCATION AND DESCRIPTION OF THE STUDIED AREA

The study area is located in the municipality of Caçapava do Sul 6.621,240mN and 260,050mE, at an altitude of 444 meters. Distant approximately 255 km from the capital of Rio Grande do Sul, Porto Alegre. The main access roads to the municipality are the federal highways BR-290, which connects Porto Alegre to Caçapava do Sul and the BR-392 which connects Santana da Boa Vista to Caçapava do Sul.

Carbonatites, in the study area (Figure 1), are intrusive in the rocks of the Passo Feio Complex. It consists of sequences of pelitic rocks, amphibolites, metavolcanoclastic, metavolcanic rocks, marbles, calcisilitic rocks, quartzite, shale and metamorphosed feldspar quartz rocks (Ribeiro et al., 1966; Bitencourt, 1983; Lopes et al., 2015). The metamorphic events (M1 and M2) that affected the region range from green shale facies to amphibolite facies, with an increase in the metamorphic degree towards granitic intrusions (for example, Granite Caçapava do Sul). Bitencourt (1983) suggests that M1 is associated with low pressure and retrogradation in M2, with a lower temperature than the M1 event. At the same time, three deformational events are described by the author: D1 and D2, which were concomitant with metamorphic events and D3, which was responsible for the uplift and generation of the antiform structure, whose core is occupied by Caçapava do Sul Granite.

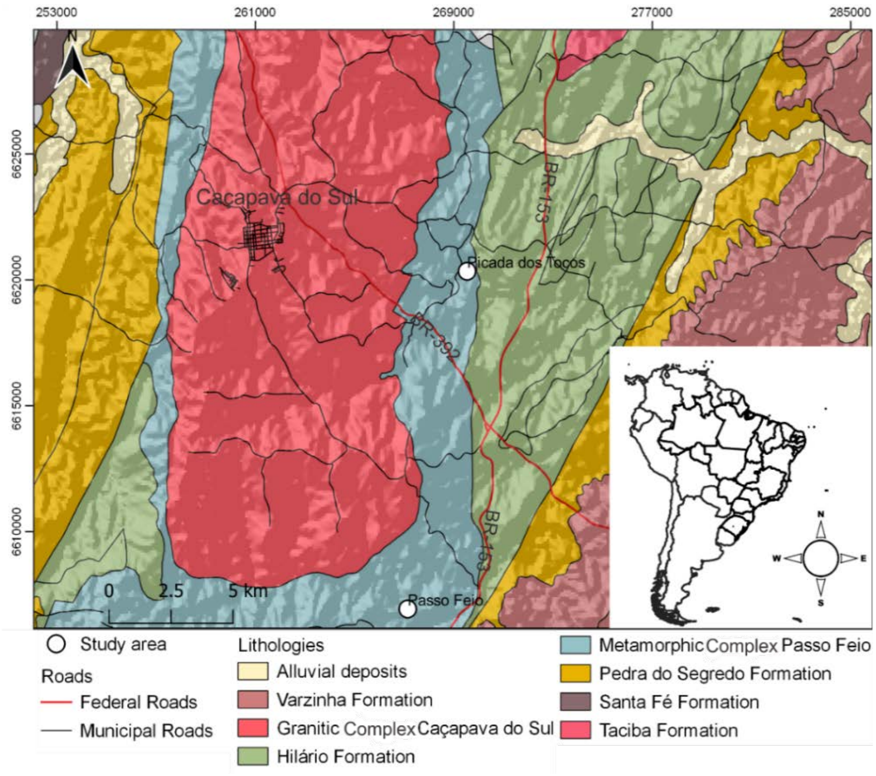

Figure 1 - Location map of the study area, Caçapava do Sul, RS.

The carbonatite Picada dos Tocos is controlled by NS failure, while the Passo feio occurrence is controlled by NE and NW failures (Cerva-Alves et al., 2017). In the Picada dos Tocos occurrence, the carbonatites have a tabular shape and are deformed together with the embedding. They are bodies approximately 2.2 km long and 80 m wide, plunging to the southeast (N110W/40W to 60W), in agreement with the regional schistosity (Rocha et al., 2013).

The carbonatite Picada dos Tocos is composed of alvikitos and beforsitos (Cerva-Alves et al., 2017). The alvikites are pink in color, with a predominance of calcite. Accessory minerals are apatite, magnetite, ilmenite, rutile, zircon, badeleite, barite, torite, pyrochlorine and minerals rich in rare earth elements (pyrochlorine, rich in Nb and Th, bastnaesite and alanite). Pyrite, chalcopyrite, chlorite, hematite, quartz and biotite are also present in different proportions, in the matrix or as stockwork. Beforsite is not outcrop, however, it is whitish, composed of approximately 80% dolomite and has the same accessory minerals and trace as alvikites (Cerva-Alves et al., 2017).

Passo Feio carbonatite has only one outcrop in flagstone and is characterized by alvikites banded with calcite, apatite, ilmenite and magnetite, in addition to levels enriched in tremolite (Cerva-Alves et al., 2017). Associated with carbonatite bodies there are rocks called titanite hornblende granofels, with a geophysical signature (eTh) similar to the Picada dos Tocos occurrence, inserted in the same geological unit.

In the mafic bands described within the carbonatite packages, a matrix composed of biotite, amphibole (actinolite > cumingtonite) and relic diopside crystals predominate. Calcite, magnetite, ilmenite, rutile, apatite, pyrite and chalcopyrite are present to a lesser extent. These rocks are milonitized and hydrothermalized, as indicated by the frequent presence of veins and stockworks of calcite, specular chlorite and pyrite / chalcopyrite and quartz, mainly close to the NW directional failures (Cerva-Alves et al., 2017).

MATERIALS AND METHOD

Soil sampling was performed in a systematic way consisting of samplimg in two areas surrounding Caçapava do sul city, one Picada dos Tocos Carbonatite and another Passo Feio Carbonatite (Figure 2). Thirty and four (PS1 – PS34) samples were collected in Picada dos Tocos Carbonatite area and twenty and eight (PS35-PS62) samples were collected in Passo Feio Carbonatite area, totaling sixty and two soil samples of 30 cm depth each (Mazhari et al., 2018; Reimann & Garett, 2005; Dung et al., 2013). For the packing were used plastic bags properly

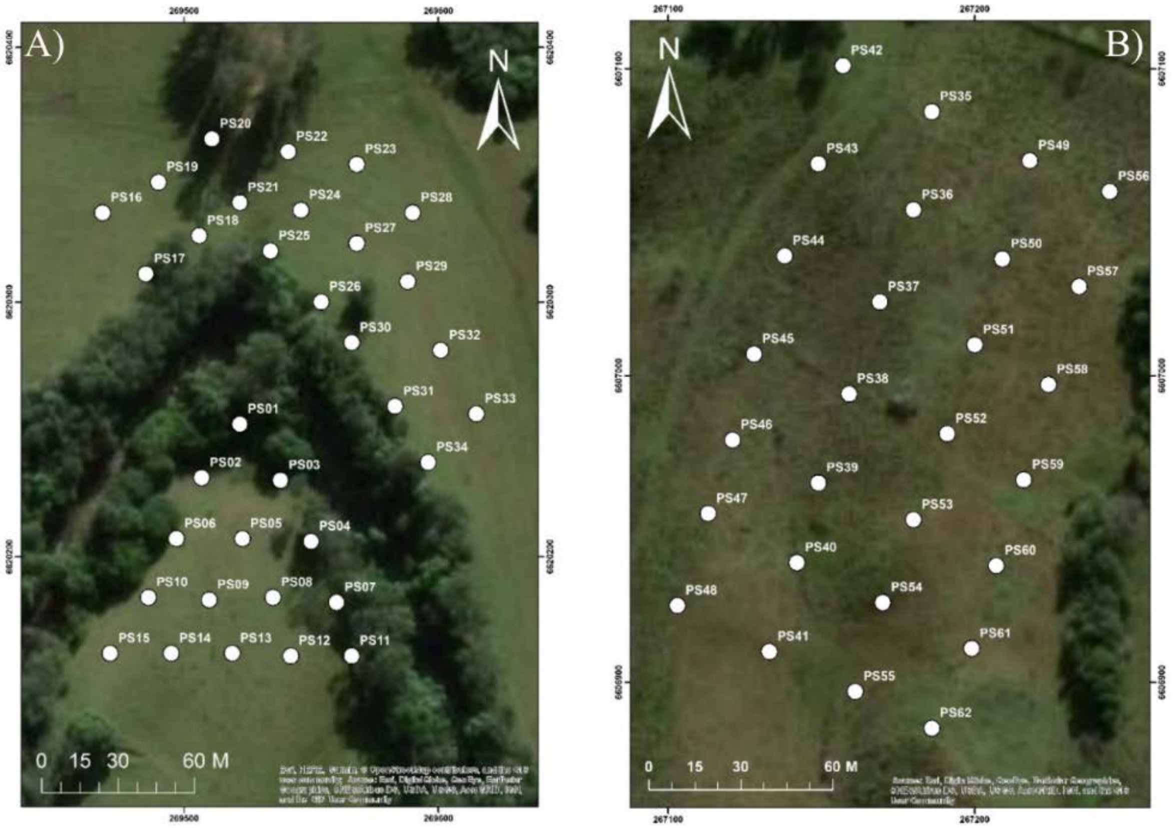

Figure 2 - Location of sampling points; (a) Picada dos Tocos Carbonatite soil samples, (b) Passo Feio Carbonatite soil samples.

labeled and identified according to the collection point number and their respective depth (Embrapa, 2006; Gomes et al. 2018; 2019). Our sample grid was regularly spaced (equally spaced lines were established), as Flatman & Yfantis (1984) and Wollenhaupt & Wolkowski (1994) recommend for geostatistical methods.

For the drying process, the samples were transferred to polypropylene containers and allowed to dry at room temperature for three days (Brasil, 2009). After drying the samples were disaggregated in porcelain grade to obtain a uniform appearance (Bini et al., 2011). About 500 g of soil sample was quartered manually to promote splits in halves successively until the desired sample size was reached. Thus, about 50 g of each sample was separated for the EDRXF analyzes.

The EDRXF analyzes were carried out in the Laboratório de Lavra, Planejamento e Tratamento de Minérios (LATRAM) at Unipampa. Each sample was subjected to readings in triplicates. The following equipment conditions were selected: tube voltage of 15 keV (Na to Sc) and 50 keV (Ti to U), with a current in the tube of 184 and 25 μA, respectively; 10 mm collimator; 120 s of real-time integration. The equipment uses an Ag anode, which allows the measuring of 25 elements, and a detector of 10 mm2 with thermoelectric cooling and resolution of ~145 eV to MnKα that maintains a speed of 100.000 counts per second (Bona et al., 2007; Teixeira et al., 2017; Wastowski et al., 2013; Gomes et al., 2020).

The Principal Component Analysis (PCA) method was used as a multivariate statistical technique. This method is commonly used to investigate the variability in large geochemical data sets (Linhai Jing & Panahi, 2006; Scheib et al., 2011; Zuo, 2011; Ueki & Iwamori, 2017).

RESULTS AND DISCUSSIONS

Energy dispersive X-Ray fluorescence (EDXRF)

The results obtained from qualitative geochemistry of soil in the samples from the area around the Picada dos Tocos and Passo Feio carbonatites soils are presented in Tables 1 and 2, respectively.

During the qualitative geochemical analysis of the samples in this study, greater attention was paid to the chemical elements Ca, Fe, Mg, Ti, P, Mn, Co, Th and Ce present in the minerals described by Cerva-Alves et al. (2017) for carbonatites in the region of Caçapava do Sul. According to Cerva-Alves (2017), the Caçapava do Sul carbonatites show two principal phases: one start with alvikite (rich Ca) and one after with beforsite (rich Mg). This suggests that these minerals and, consequently, their chemical compositions in the soil are prospective indicators of carbonatite rocks.

In terms of elements, the Si, Mg, Al, K, Rh, Cd values obtained are higher in Picada dos Tocos Carbonatite soil than in Passo Feio Carbonatite soil. However, the concentration of P, Cl, Ca, Ti, Mn, Fe, Co, Ce and Th values are higher in Passo Feio Carbonatite soil than in Picada dos Tocos Carbonatite soil. The uranium was only detected in Passo Feio Carbonatite soil especially in the samples PS41, PS48, PS54 and PS57.

It is important to note that the Ce values in Passo Feio Carbonatite soil (Figure 3) confirms once again that this soil is being enriched with the weathering of the source rock rich in minerals rich in Th and Ce such as monazites and other minerals that contain rare earth elements (bastnaesite) (Cerva-Alves et al., 2017). Due to the low mobility of the P element and its impoverishment caused by the transport of liquids. It can be an excellent identifier of carbonatite rocks as it is extremely rich in primary minerals such as apatite. Fe has high concentrations, mainly due to the presence of magnetite and hematite in the rocks that provided this element to carbonatitic magma. Thus, generating considerable anomalies when compared to the contents of the area close to the outcrop (Figure 3).

The deformation observed in the Passo Feio Carbonatite (outcrop in the PS54), its proximity to large structures and its concordant relationship with the embedding (Rocha et al., 2013), support the hypothesis that this occurrence corresponds to a linear type carbonatite, according to classification by Lapin & Ploshko (1988). The elements P, Fe and Co are very important for determining the area of influence of the carbonatite body that follows a central-south pattern (Figure 3).

One can clearly see the positive correlations between Ti, Fe, Mn and Co in the Carbonatito Picada dos Tocos (Figure 4) which according to Cerva-Alves et al. (2017) are elements that have their high values due to the enrichment caused by

Table 1 - Major elements and traces from the analyzed soils in Picada dos Tocos Carbonatite area.

Sample	Mg	Al	Si	P	Cl	K	Ca	Ti	Mn	Fe	Co	Rh	Cd	Ce	Th
PS1	3.67	7.52	31.7	Nd	0.09	1.66	7.26	0.19	0.03	1.81	0.08	0.33	Nd	0.08	Nd
PS2	4.64	9.84	41.8	Nd	0.09	2.21	3.69	0.15	0.03	1.36	0.07	0.26	0.09	0.12	Nd
PS3	4.49	10.2	40.8	Nd	0.08	2.33	1.19	0.24	0.03	1.55	0.07	0.29	0.12	Nd	Nd
PS4	6.09	9.41	39.1	0.06	0.08	2.40	0.99	0.25	0.03	1.35	0.06	0.29	0.11	0.08	Nd
PS5	1.79	13.1	52.9	Nd	0.07	2.83	1.23	0.45	0.04	2.05	0.10	0.19	0.08	0.10	Nd
PS6	1.54	8.92	36.8	Nd	0.08	2.30	1.09	0.43	0.03	1.85	0.08	0.35	0.16	0.16	Nd
PS7	2.97	9.82	36.3	Nd	0.07	1.97	1.09	0.34	0.04	1.82	0.07	0.34	0.12	0.10	Nd
PS8	3.78	9.41	41.5	0.06	0.09	2.41	1.01	0.58	0.06	2.39	0.11	0.28	0.13	0.21	0.07
PS9	5.87	9.87	41.4	Nd	0.09	2.29	0.82	0.56	0.04	2.04	0.09	0.28	0.10	0.18	0.04
PS10	4.44	8.26	33.4	Nd	0.08	2.40	1.00	0.36	0.03	1.66	0.07	0.34	Nd	0.15	Nd
PS11	3.10	13.7	49.4	Nd	0.07	2.51	1.20	0.41	0.06	2.26	0.12	0.21	0.09	0.09	0.03
PS12	2.94	8.39	35.7	Nd	0.09	1.78	0.71	0.62	0.06	2.21	0.09	0.36	0.13	0.14	Nd
PS13	3.28	11.7	53.7	Nd	0.08	1.95	0.73	0.80	0.05	2.76	0.15	0.19	0.08	0.16	Nd
PS14	4.24	8.62	37.6	Nd	0.07	1.93	0.91	0.40	0.04	2.08	0.09	0.32	Nd	0.18	Nd
PS15	4.65	7.66	29.0	Nd	0.09	1.88	2.45	0.28	0.03	1.90	0.08	0.37	0.13	0.18	Nd
PS16	5.74	9.96	50.3	Nd	0.10	0.56	0.77	2.41	0.11	7.11	0.43	0.15	0.06	0.26	Nd
PS17	4.76	8.18	24.3	0.02	0.08	0.55	0.85	2.15	0.16	8.79	0.38	0.29	0.15	0.29	0.13
PS18	2.49	6.92	24.0	0.04	0.09	0.63	1.16	2.67	0.17	10.0	0.44	0.29	0.13	0.29	0.17
PS19	5.67	5.99	33.4	Nd	0.09	0.43	0.59	1.95	0.11	5.58	0.27	0.31	0.14	0.30	Nd
PS20	4.70	7.96	35.7	Nd	0.09	0.44	0.74	1.56	0.13	6.34	0.31	0.27	0.10	0.29	0.1
PS21	4.35	9.19	46.8	Nd	0.09	0.87	0.75	1.85	0.09	4.70	0.25	0.20	0.08	0.27	Nd
PS22	5.69	6.25	25.3	Nd	0.09	0.43	0.67	1.38	0.08	4.59	0.20	0.34	0.16	0.28	0.16
PS23	3.77	10.9	55.8	Nd	0.08	0.98	0.84	1.73	0.11	4.83	0.28	0.15	0.08	0.19	0.21
PS24	5.77	7.09	34.4	0.17	0.09	0.72	1.58	1.69	0.13	5.72	0.26	0.26	0.11	0.34	Nd
PS25	5.05	9.37	37.5	0.2	0.08	0.92	1.41	1.98	0.15	6.45	0.33	0.22	0.10	0.22	Nd
PS26	1.18	5.45	28.8	0.35	0.08	0.53	1.86	2.14	0.16	6.32	0.24	0.30	0.12	Nd	Nd
PS27	6.93	6.04	23.6	0.13	0.09	0.56	1.43	2.81	0.20	9.17	0.41	0.28	0.14	0.36	0.35
PS28	4.45	8.56	32.8	0.12	0.09	0.53	0.91	2.10	0.18	7.24	0.34	0.25	0.11	0.37	0.44
PS29	2.49	9.87	42.5	0.39	Nd	0.63	2.09	3.09	0.24	9.32	0.52	0.16	Nd	0.25	Nd
PS30	6.30	10.2	34.1	0.29	0.08	1.12	2.96	3.24	0.22	11.2	0.62	0.14	0.06	0.10	Nd
PS31	2.72	4.1	15.8	0.71	0.10	0.29	3.35	2.28	0.21	9.03	0.34	0.27	0.11	0.38	Nd
PS32	6.09	7.69	33.6	0.16	0.09	0.85	1.79	2.10	0.15	6.51	0.33	0.26	0.11	0.30	0.53
PS33	6.83	8.41	40.8	0.08	0.09	1.11	1.13	1.67	0.13	5.05	0.27	0.21	0.08	0.27	Nd
PS34	2.98	5.28	22.3	0.31	0.09	0.53	2.19	2.91	0.21	9.50	0.41	0.25	0.12	0.42	Nd

Note: Nd= Value minor than the detection threshold

the presence of the rock in the place. Taking into account that these elements have mobility considered low and, in some cases, very low, it is possible to visualize a common area where all these elements present higher values, considered anomalous with those found in the vicinity, being a good indicator of what is the area of influence of the rock in the soil.

The Picada dos Tocos Carbonatite outcropping in the PS31 is present in the central-eastern portion of the study area and has a northeast behavior regarding its main area of influence in the soil. This behavior is linked to the topography of the area and the way the body intruded into the rock.

Statistical analysis

The concept of correlation refers to a numerical association between two variables, not necessarily implying a cause and effect relationship or even the existence of a structure with practical interests. Correlation analysis was obtained using Pearson's correlation coefficient (R), which is a bivariate correlation. The variables that present $r > 0.7$ are considered strongly correlated, while $r > 0.5$-0.7 shows moderate correlation at a significant level ($P \leq 0.05$ with a confidence level of 95%; Table 3; Mukaka, 2012), positive or negative. Sillanpãã (1972) and Alloway et al. (1990), suggest that the total content and its correlations in the source material reflect its content in the sediments.

Table 3 shows the samples from Picada dos Tocos Carbonatite soil strong positive correlations between **Al** and Si (0.87); **P** and Mn (0.73); **Ti** and Mn (0.96), Fe (0.97), Co (0.97); **Mn** and Fe (0.97), Co (0.93), **Fe** and Co (0.97) and, **Rh** and Sb (0.74). Moderate positive correlations are observed for **Al** and K (0.64); **P** and Ti (0.59), Fe (0.62), Co (0.53); **Ce** and Ti (0.62), Mn (0.61), Fe (0.62), Co (0.56), Mo (0.51). In addition, it demonstrates strong negative correlations between **Si** and Sb (-0.73); **K** and Ti (-0.85), Mn (-0.81), Fe (-0.83), Co (-0.79), Ce (-0.70). Whereas, moderate negative correlations

Table 2 - Major elements and traces from the analyzed soils in Passo Feio Carbonatite area.

Sample	Mg	Al	Si	P	Cl	K	Ca	Ti	Mn	Fe	Co	Rh	Cd	Ce	Th	U
PS35	7.08	8.08	31.0	Nd	0.10	1.15	0.15	0.92	0.09	5.57	0.26	0.29	0.09	0.47	Nd	Nd
PS36	3.07	14.8	51.3	0.05	0.08	1.51	0.56	1.86	0.15	8.02	0.48	0.05	0.06	0.19	0.05	Nd
PS37	5.05	5.39	17.8	0.15	0.10	1.19	2.31	3.27	0.22	11.0	0.49	0.25	0.13	0.35	Nd	Nd
PS38	4.53	6.41	20.5	0.29	0.10	1.16	2.72	2.58	0.22	9.79	0.43	0.25	0.12	0.47	0.49	Nd
PS39	1.42	6.94	22.3	0.31	0.10	1.23	4.13	3.27	0.24	10.9	0.50	0.20	0.08	0.41	0.41	Nd
PS40	3.81	4.95	17.2	0.31	0.10	1.04	4.53	3.39	0.21	10.5	0.47	0.24	Nd	0.28	0.54	Nd
PS41	6.04	6.37	19.9	0.3	0.09	0.78	4.11	3.25	0.24	12.0	0.57	0.21	0.11	0.35	0.44	0.21
PS42	5.22	9.08	32.5	0.11	0.08	0.59	0.40	1.07	0.18	7.97	0.38	0.28	0.09	0.46	Nd	Nd
PS43	3.81	12.7	47.2	Nd	0.10	1.60	0.19	1.17	0.13	6.57	0.38	0.18	0.09	0.38	0.02	Nd
PS44	4.61	8.91	34.6	Nd	0.10	1.07	0.22	1.00	0.12	5.29	0.25	0.31	0.13	0.45	Nd	Nd
PS45	3.91	9.2	36.7	Nd	0.09	1.26	0.39	1.11	0.11	5.94	0.29	0.28	0.11	0.4	Nd	Nd
PS46	3.66	12.3	45.6	0.13	0.09	1.76	1.06	2.33	0.20	9.31	0.55	0.15	0.06	0.27	Nd	Nd
PS47	3.11	5.44	20.8	0.34	0.09	0.86	2.55	2.33	0.25	10.5	0.47	0.28	0.12	0.69	0.74	Nd
PS48	6.07	5.47	17.2	0.36	0.09	1.22	3.50	2.82	0.21	10.2	0.43	0.24	0.14	0.21	0.46	0.31
PS49	3.75	8.99	40.4	Nd	0.10	1.04	0.45	1.71	0.13	6.64	0.34	0.25	0.1	0.39	0.14	Nd
PS50	3.62	5.44	19.6	0.33	0.10	1.04	2.06	3.00	0.27	11.2	0.50	0.27	0.14	0.4	0.70	Nd
PS51	3.63	8.51	28.3	0.42	0.10	1.18	3.35	2.97	0.25	11.2	0.56	0.18	0.08	0.57	Nd	Nd
PS52	3.92	7.18	24.7	0.35	0.10	1.01	5.91	3.61	0.23	10.9	0.54	0.18	0.08	0.26	0.36	Nd
PS53	5.34	5.89	20.2	0.56	0.09	0.59	6.69	3.31	0.23	12.9	0.61	0.14	0.08	0.10	Nd	Nd
PS54	3.49	6.91	22.1	1.21	0.11	1.02	7.99	4.18	0.26	13.7	0.73	0.15	0.10	0.10	0.43	0.17
PS55	3.55	5.12	19.1	0.50	0.10	0.67	6.34	4.17	0.24	12.6	0.58	0.20	0.10	0.10	0.42	Nd
PS56	1.16	10.5	38.8	0.60	0.10	1.21	3.16	3.33	0.26	10.0	0.54	0.15	0.07	0.21	0.40	Nd
PS57	5.05	6.64	17.8	0.38	0.09	1.41	3.00	2.50	0.27	12.2	0.55	0.22	0.13	0.25	0.40	0.21
PS58	2.42	5.37	16.3	0.46	0.10	0.66	4.12	3.20	0.21	9.56	0.38	0.25	Nd	0.25	0.53	Nd
PS59	Nd	4.42	18.0	0.30	0.07	0.49	4.61	3.70	0.20	10.0	0.39	0.27	0.12	0.06	Nd	Nd
PS60	Nd	6.53	28.4	0.55	0.08	1.36	6.20	4.16	0.24	12.0	0.59	0.17	0.09	Nd	0.39	Nd
PS61	2.86	5.83	19.3	0.35	0.08	0.76	3.29	2.43	0.22	10.0	0.44	0.27	0.12	0.62	0.40	Nd
PS62	2.56	5.33	17.0	0.71	0.10	0.56	5.70	3.28	0.24	12.3	0.54	0.21	0.14	0.28	Nd	Nd

Note: Nd= Value minor than the detection threshold

are observed between **Al** and Sb (-0.68), Ce (-0.53); **Si** and Mo (-0.50), Rh (-0.56); **Co** and Rh (-0.56).

The samples from Passo Feio Carbonatite soil (Table 4) show strong positive correlations between **Al** and Si (0.96); **P** and Ca (0.86), Ti (0.77), Mn (0.73), Fe (0.81), Co (0.78); **Ca** and Ti (0.90), Mn (0.70), Fe (0.86), Co (0.75); **Ti** and Mn (0.80), Fe (0.88), Co (0.78); **Mn** and Fe (0.92), Co (0.82); **Fe** and Co (0.90); **Rh** and Sb (0.76). Moderate positive correlations are observed between **Al** and K (0.65); Si and K (0.61); **Mo** and Ti (0.58), Ca (0.54), Mn (0.54), Fe (0.50); **Th** and Mn (0.59), Mo (0.55); **Rh** and Ce (0.52). Strong negative correlations occur between **Mo** and Al (-0.72), Si (-0.75). Whereas moderate negative correlations were observed between **Al** and Ca (-0.60), Ti (-0.57), Mn (-0.50), Fe (-0.56), Sb (-0.56); **Si** and Ca (-0.63), Ti (-0.59), Mn (-0.60), Fe (-0.65), Sb (-0.53), Th (-0.50); Ce and Ca (-0.56), Ti (-0.57); Rh and Co (-0.66).

The main ion exchanges correlate with the correlation coefficients found within the same order. Therefore, it is possible that the simultaneous increase or decrease in cations is the result, mainly, of ion exchange effects in the mineral assemblage of the sediment investigated.

For a better understanding of the geochemical properties of the investigated soil samples, Principal Component Analysis (PCA) was applied based on the correlation matrix between the components and the standardized variables. In the same way, as in Pearson correlation matrix, the data of water samples investigated for each soil area were interpreted separately.

Therefore, in the Picada dos Tocos Carbonatite soil, 10 PCs represent 100% of the variance

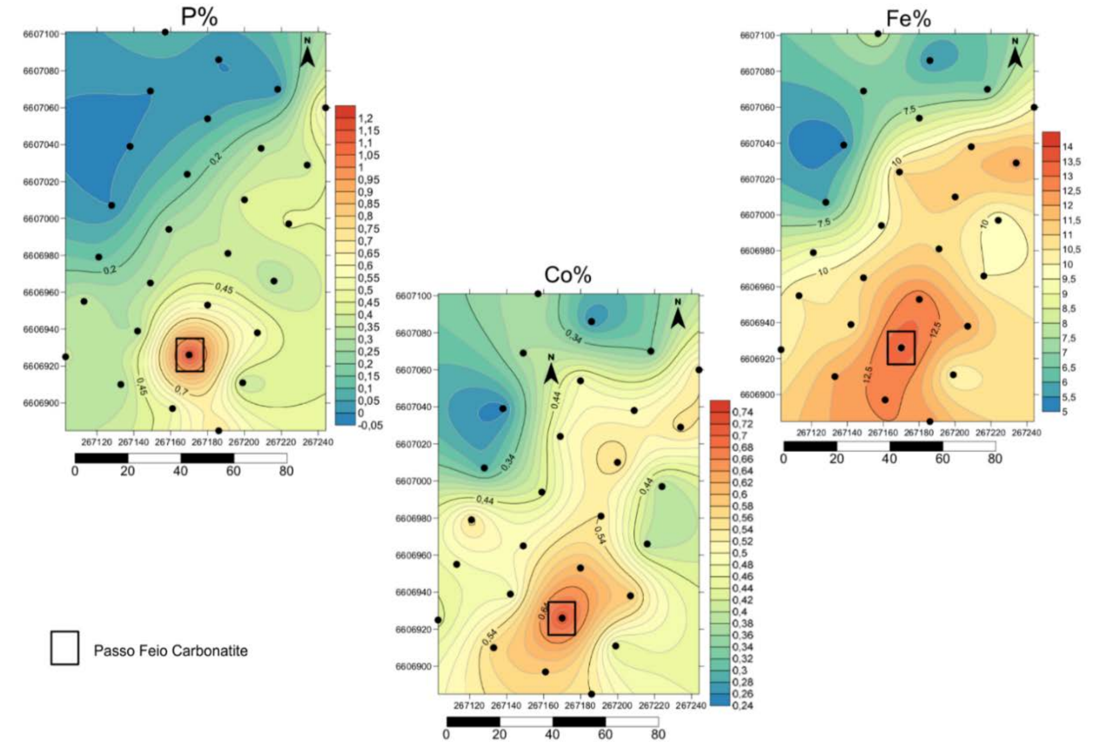

Figure 3 - Isoline maps with P, Co, and Fe content (%) in the soil near Passo Feio Carbonatite area.

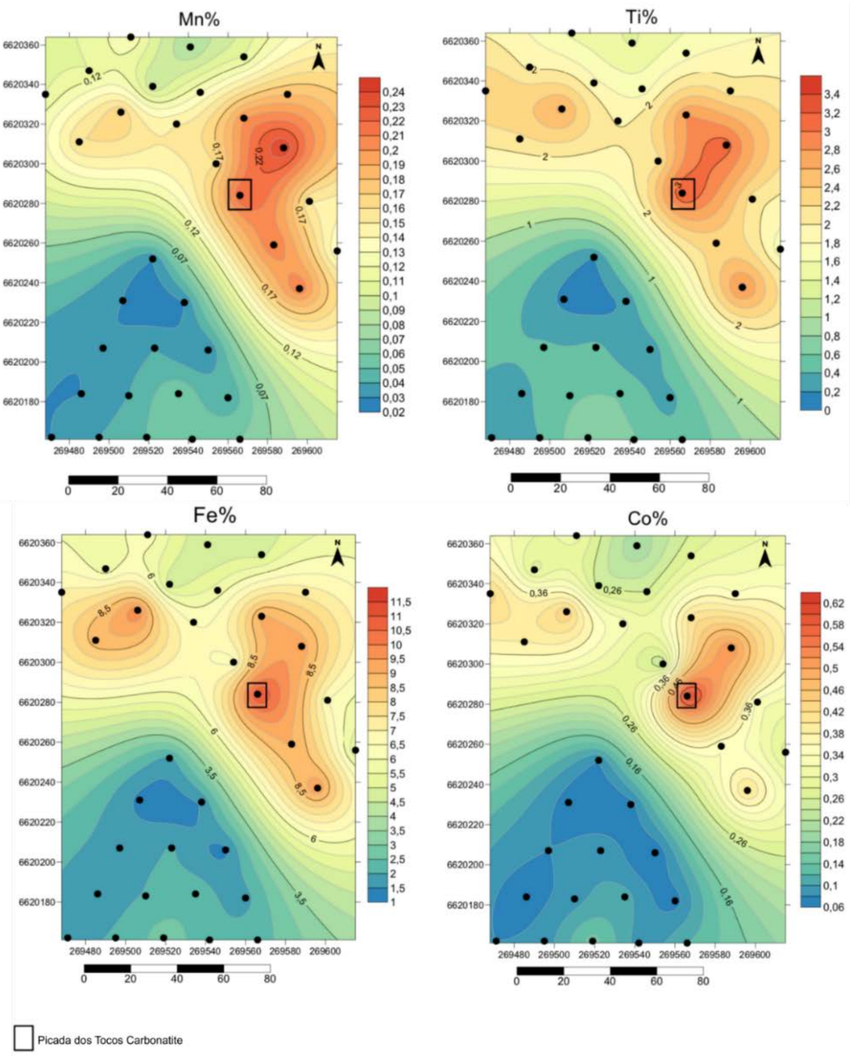

Figure 4 - Isoline maps with Fe, Ti, Mn and Co content (%) in the soil near Picada dos Tocos Carbonatite area.

Table 3 – Pearson correlation for elements investigated in soil from Picado dos Tocos Carbonatite.

	Mg	Al	Si	P	Cl	K	Ca	Ti	Mn	Fe	*Co	*Rh	*Cd	*Ce	*Th
Mg	1.00	-0.10	-0.05	-0.18	0.33	-0.20	-0.10	0.15	0.08	0.13	0.20	-0.11	0.03	0.28	0.28
Al	-0.10	1.00	**0.87**	-0.46	-0.36	**0.64**	-0.21	-0.41	-0.43	-0.44	-0.27	-0.48	-0.30	**-0.53**	-0.17
Si	-0.05	**0.87**	1.00	-0.47	-0.27	0.48	-0.27	-0.35	-0.44	-0.46	-0.28	**-0.56**	-0.36	-0.42	-0.20
P	-0.18	-0.46	-0.47	1.00	-0.17	-0.48	0.31	**0.59**	**0.73**	**0.62**	**0.53**	-0.23	-0.04	0.32	-0.01
Cl	0.33	-0.36	-0.27	-0.17	1.00	-0.12	0.03	-0.08	-0.15	-0.05	-0.13	0.26	0.43	0.22	0.17
K	-0.20	**0.64**	0.48	-0.48	-0.12	1.00	0.01	**-0.85**	**-0.81**	**-0.83**	**-0.79**	0.20	-0.18	**-0.70**	-0.36
Ca	-0.10	-0.21	-0.27	0.31	0.03	0.01	1.00	-0.05	0.05	0.03	0.00	0.07	-0.36	-0.16	-0.14
Ti	0.15	-0.41	-0.35	**0.59**	-0.08	**-0.85**	-0.05	1.00	**0.96**	**0.97**	**0.97**	-0.48	0.07	**0.62**	0.33
Mn	0.08	-0.43	-0.44	**0.73**	-0.15	**-0.81**	0.05	**0.96**	1.00	**0.97**	**0.93**	-0.43	0.06	**0.61**	0.35
Fe	0.13	-0.44	-0.46	**0.62**	-0.05	**-0.83**	0.03	**0.97**	**0.97**	1.00	**0.97**	-0.41	0.10	**0.63**	0.33
***Co**	0.20	-0.27	-0.28	**0.53**	-0.13	**-0.79**	0.00	**0.97**	**0.93**	**0.97**	1.00	**-0.56**	-0.02	**0.57**	0.31
***Rh**	-0.11	-0.48	**-0.56**	-0.23	0.26	0.20	0.07	-0.48	-0.43	-0.41	**-0.56**	1.00	0.34	-0.11	-0.03
***Cd**	0.03	-0.30	-0.36	-0.04	0.43	-0.18	-0.36	0.07	0.06	0.10	-0.02	0.34	1.00	0.23	0.25
***Ce**	0.28	**-0.53**	-0.42	0.32	0.22	**-0.70**	-0.16	**0.62**	**0.61**	**0.63**	**0.57**	-0.11	0.23	1.00	0.44
***Th**	0.28	-0.17	-0.20	-0.01	0.17	-0.36	-0.14	0.33	0.35	0.33	0.31	-0.03	0.25	0.44	1.00

Table 4 – Pearson correlation for elements investigated in soil from Passo Feio Carbonatite.

	Mg	Al	Si	P	Cl	K	Ca	Ti	Mn	Fe	*Co	*Rh	*Cd	*Ce	*Th	*U
Mg	1.00	0.03	-0.04	-0.31	0.25	0.05	-0.32	-0.45	-0.29	-0.20	-0.20	0.23	0.19	0.31	-0.15	0.40
Al	0.03	1.00	**0.96**	-0.43	-0.05	**0.65**	**-0.60**	**-0.57**	**-0.50**	**-0.56**	-0.18	-0.49	-0.24	0.07	-0.47	-0.19
Si	-0.04	**0.96**	1.00	**-0.50**	-0.08	**0.61**	**-0.63**	**-0.59**	**-0.60**	**-0.65**	-0.28	-0.38	-0.21	0.06	**-0.50**	-0.30
P	-0.31	-0.43	**-0.50**	1.00	0.25	-0.32	**0.86**	**0.77**	**0.73**	**0.81**	**0.78**	-0.34	-0.01	-0.44	0.39	0.29
Cl	0.25	-0.05	-0.08	0.25	1.00	0.13	0.11	0.10	0.08	0.07	0.13	0.00	-0.12	0.13	0.19	-0.01
K	0.05	**0.65**	**0.61**	-0.32	0.13	1.00	-0.43	-0.29	-0.22	-0.29	-0.01	-0.37	-0.09	0.02	-0.10	0.09
Ca	-0.32	**-0.60**	**-0.63**	**0.86**	0.11	-0.43	1.00	**0.90**	**0.70**	**0.86**	**0.75**	-0.33	-0.08	**-0.57**	0.36	0.21
Ti	-0.45	**-0.57**	**-0.59**	**0.77**	0.10	-0.29	**0.90**	1.00	**0.80**	**0.88**	**0.78**	-0.36	-0.11	-0.58	0.44	0.16
Mn	-0.29	**-0.50**	**-0.60**	**0.73**	0.08	-0.22	**0.70**	**0.80**	1.00	**0.92**	**0.82**	-0.26	0.08	-0.20	**0.59**	0.26
Fe	-0.20	**-0.56**	**-0.65**	**0.81**	0.07	-0.29	**0.86**	**0.88**	**0.92**	1.00	**0.90**	-0.37	0.06	-0.41	0.44	0.31
***Co**	-0.20	-0.18	-0.28	**0.78**	0.13	-0.01	**0.75**	**0.78**	**0.82**	**0.90**	1.00	**-0.66**	-0.05	-0.45	0.31	0.27
***Rh**	0.23	-0.49	-0.38	-0.34	0.00	-0.37	-0.33	-0.36	-0.26	-0.37	**-0.66**	1.00	0.35	**0.52**	0.11	-0.05
***Cd**	0.19	-0.24	-0.21	-0.01	-0.12	-0.09	-0.08	-0.11	0.08	0.06	-0.05	0.35	1.00	0.20	-0.06	0.31
***Ce**	0.31	0.07	0.06	-0.44	0.13	0.02	**-0.57**	**-0.58**	-0.20	-0.41	-0.45	**0.52**	0.20	1.00	0.05	-0.21
***Th**	-0.15	-0.47	**-0.50**	0.39	0.19	-0.10	0.36	0.44	**0.59**	0.44	0.31	0.11	-0.06	0.05	1.00	0.28
***U**	0.40	-0.19	-0.30	0.29	-0.01	0.09	0.21	0.16	0.26	0.31	0.27	-0.05	0.31	-0.21	0.28	1.00

of the obtained results (Table 5). The first three PCs are > 1, representing 80.75% of the variance (Table 5; Figure 5). For the soil samples of the Passo Feio Carbonatite soil, 10 PCs represent 100% of the variance in the results obtained (Table 5). The first three PCs presented values higher than 1, representing 83.98% of the variance (Table 5; Figure 5). The first and second principal components (PC1 and PC2) of the samples investigated from Picada dos Tocos Carbonatite soil are the result of the linear combination of 15 variables studied, and both PCs explained 48.85% and 17.31% of the variance, respectively (Table 5). On the other hand, PC1 and PC2 of the samples investigated from Passo Feio Carbonatite soil are the results of the linear combination of 16 variables studied, and both PCs explained 55.93% and 15.38% of the variance, respectively (Table 5).

The PCA also produces eigenvectors, coefficients or charges of principal components (Figure 5). According to Reimann et al. (2008), the eigenvectors describes the relative importance of a component. For example, a chemical element and its variability between a data group. Thus, the grouping of high-load elements provides high scores, and the grouping of low-payload elements provides low scores.

In the Picada dos Tocos Carbonatite soil, the highest scores of PC1 with a variation of 48.86% are represented by Si, Al and K (Figure 5A), being the lowest rate equivalent to Rh. For PC2, the highest scores are equivalent Mg, Cl, Ca, and Co, in that Th, Ce shows numbers lower than 0.19.

For PC1 (variation of 56.94%) of the elements and parameters of Passo Feio Carbonatite soil, high scores are commensurate to high load elements (> 0.2), for example, Si, Al, K, Mg and Ce (Figure 5B). The lowest scores are equivalent to the lowest rates (< 0.19), such as Rh. High scores for PC2 are related to strong positive loads (> 0.2) for Cd, with low rates related to U, Cl and Th (Figure 5B).

Table 5 - Eigenvalues of correlation matrix and related statistics of the water from Picada dos Tocos and Passo Feio Carbonatites soils.

PCs (Picada dos Tocos Caronatite soil)	Eigenvalue	Total variance %	Cumula-tive Eigenvalue	Cumulative %	PCs (Passo Feio Carbo-natite soil)	Eigenvalue	Total Variance %	Cumulative Eigenvalue	Cumulative %
1	4.885990	48.85990	4.88599	48.8599	1	5.593629	55.93629	5.59363	55.9363
2	1.731995	17.31995	6.61798	66.1798	2	1.538590	15.38590	7.13222	71.3222
3	1.457285	14.57285	8.07527	80.7527	3	1.266714	12.66714	8.39893	83.9893
4	0.775992	7.75992	8.85126	88.5126	4	0.638775	6.38775	9.03771	90.3771
5	0.486164	4.86164	9.33743	93.3743	5	0.452093	4.52093	9.48980	94.8980
6	0.359891	3.59891	9.69732	96.9732	6	0.266371	2.66371	9.75617	97.5617
7	0.219743	2.19743	9.91706	99.1706	7	0.164140	1.64140	9.92031	99.2031
8	0.056058	0.56058	9.97312	99.7312	8	0.037424	0.37424	9.95773	99.5773
9	0.020260	0.20260	9.99338	99.9338	9	0.022366	0.22366	9.98010	99.8010
10	0.006622	0.06622	10.00000	100.0000	10	0.019900	0.19900	10.00000	100.0000

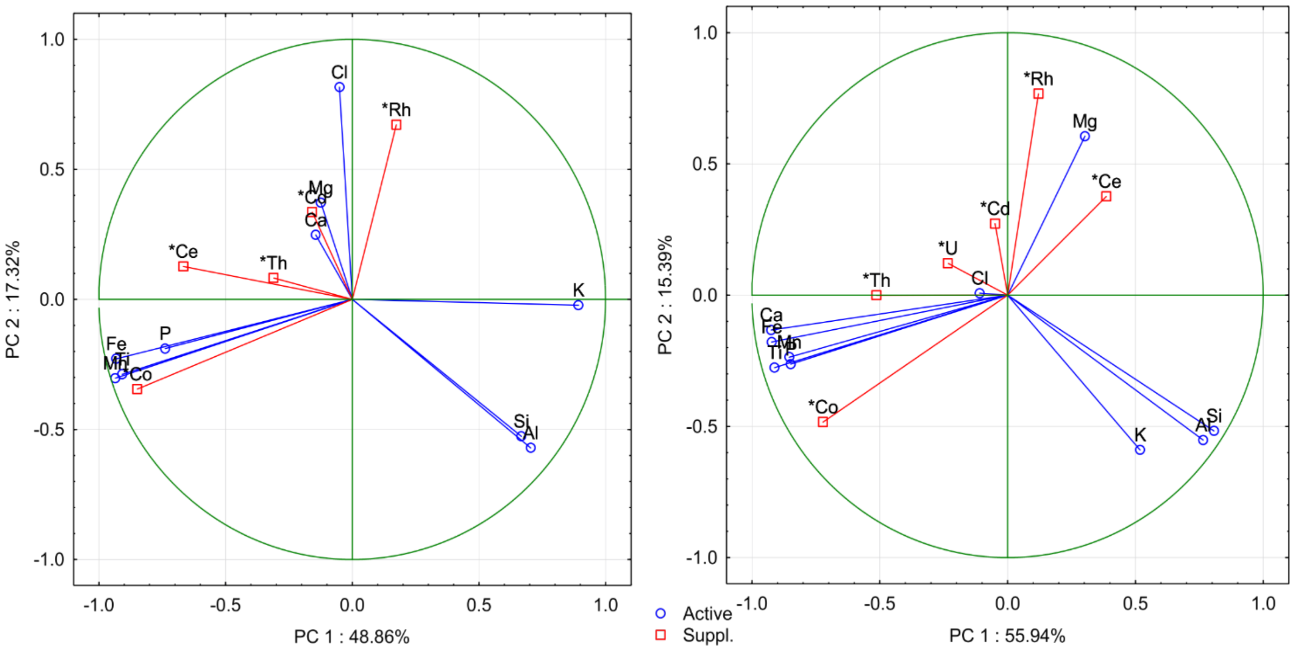

Figure 5 - Projection of the variables on the factor-plane (PC1 and PC2) from eigenvectors in (A) Picada dos Tocos Carbonatite soil and (B) Passo Feio Carbonatite soil**.**

CONCLUSION

The data provide new understanding of the chemical composition of the Picada dos Tocos and Passo Feio Carbonatites soils. Thus, it is observed that:

The soils showed high concentration of Ca, Mg, Fe, Ti, P, Mn, Co, Th and Ce. The P, Ti, Mn and Co are present in high concentrations due to the content of these elements in the chemical composition of minerals present in carbonatitic rocks. Ca and Mg anomalies are also linked to the high presence of these elements in the mineralogy of the rock alvikito (Ca) and beforsite (Mg). The high concentrations of Ce and Th are directly related to the presence of minerals rich in ETR's like monazite and bastnasite (Wall & Mariano, 1995). The Fe has high concentrations, mainly due to the presence of magnetite and hematite in the rocks that provided this element to carbonatitic magma (Le Bas, 1981).

Comparison of samples using multivariate statistical methods showed strong and positive correlations (See Table 3, Table 4 and Table 5). Thus, variations in chemical signatures and the results of multivariate statistical analysis for soils in the Picada dos Tocos region and soils in the Passo Feio region can certainly be interpreted as derived from the interaction with lithology (in particular, carbonatites). The distribution of the scores for PC1 and PC2 shows that changes can happen in the geochemistry composition of the soils. In the Picada dos Tocos Carbonatite soil, the highest scores of PC1 with a variation of 48.86% are represented by Si, Al and K, being the lowest rate equivalent to Rh. For PC2, the highest scores are equivalent Mg, Cl, Ca, and Co, in that Th, Ce shows numbers lower than 0.19. For PC1 (variation of 56.94%) of the elements and parameters of Passo Feio Carbonatite soil, high scores are commensurate to high load elements (> 0.2), for example, Si, Al, K, Mg and

Ce. The lowest scores are equivalent to the lowest rates (< 0.19), such as Rh. High scores for PC2 are related to strong positive loads (> 0.2) for Cd, with low rates related to U, Cl and Th.

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