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Geochemical signatures and weathering rates in soils derived from different granites in contrasting climatic locations

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ABSTRACT. We studied the mineralogical properties and chemical composition of different granites using energy dispersive X-ray spectroscopy coupled with scanning electron microscopy to understand the relationship between granite signatures and soil characteristics, including weathering patterns and soil fertility status. The discriminant analysis (DA) was based on soil physical and chemical properties and was used to differentiate soils developed from I- and S-type granites across contrasting climatic conditions in northeast Brazil. The DA identified the highest values of organic carbon, clay and plant nutrients as key variables to recognize soil profiles derived from I-type granites. In contrast, the greater sand contents and Al saturation distinguished soils developed from S-type granites. These results were related to the mineralogical characteristics of each granite type, such as a high percentage of silica-bearing minerals in the S-type granites. The highest concentrations of K, Ca, Mg, and P in I-type granites were found in feldspars, amphiboles, and apatite. These elements account for the majority of nutrients derived in their soil profiles. However, it seems that the harsh conditions of the humid tropical environment equalized the effect of the rocks on weathering rates-the difference in chemical index of alteration is more extreme in the dry region.

Keywords: soil science; soil genesis; soil fertility; chemical index of alteration; northeastern Brazil.

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Introduction

The mineralogical and chemical composition of granite is controlled by petrogenetic processes (Chappell & White, 2001). The subcategories of I-, S-, and A-type granites have been extensively applied in Earth science studies to geochemically classify granites and granitoids (Guani, Searle, Robb, & Chung, 2013; Guan et al., 2014; Wang et al., 2014; Foden, Sossi, & Wawryk, 2015; Litvinovsky, Jahn, & Eyal, 2015; Wang et al., 2015; Vilalva, Vlach, & Simonetti, 2016). I-type granites are derived from igneous protoliths, whereas S-type granites are mainly formed by a fusion of sedimentary rocks (Chappell & White, 2001). In turn, A-type granites (the term "A" denoting anorogenic and/or anhydrous) occur across rift zones and within stable continental blocks. The identification of A-type granites is based on both tectonic settings and chemical characteristics, while I and S types are strictly based on the difference in the rock sources (Chappell & White, 2001).

Soils developed from granitic rocks are widely distributed worldwide and cover large areas on all continents. Therefore, the knowledge of the properties of granites, which influence soil characteristics, can shed light on weathering patterns and soil properties. Although numerous studies have focused on understanding the mineralogy and chemical composition of granites, only a few have dealt with the effects of the contrasting origins and mineralogy on weathering and soil formation processes (Gontier et al., 2015; Mareschal, Turpault, & Ranger, 2015; Silva et al., 2016).

We studied I- and S-type granites in the Borborema Province in northeast Brazil. This province is in the Western portion of the extensive geologic Brasilian-Pan African orogenic system formed by the collision between the West Africa/São Luis and San Francisco-Congo Cratons (Van Schmus et al., 2008). Borborema Province covers approximately 380,000 km^2 and is marked by a mosaic of tectonic blocks: a Paleoproterozoic basement and scattered Archean nuclei, Meso to Neoproterozoic supracrustal rocks, and large intrusions of granites (Van Schmus et al., 2008; Silva, Ferreira, Lima, Sial, & Silva, 2015). Neoproterozoic magmatism in this province produced voluminous S- and I-type granites. This geological setting represents part of the Gondwana continent found in vast tropical areas such as South America, sub-Saharan Africa, India, Asia (Southeast and East) and Australia.

Multivariate statistical techniques have been widely applied to study environmental issues (Matiatos, Alexopoulos, & Ath, 2014; Zhang, Qian, Chen, & Qiao, 2014; Thivya et al., 2015; Matiatos, 2016; Taiti et al., 2016). These techniques provide information that is not available via univariate statistics. Principal component analysis (PCA) (Boteva, Radeva, Traykov, & Kenarova, 2016; Rojas, Prause, Sanzano, Arce, & Sánchez, 2016; Taboada, Rodríguez-Lado, Ferro-Vázquez, Stoops, & Cortizas, 2016), cluster analysis (CA) (Chung et al., 2015; Bitencourt et al., 2016; Nekoeinia, Mohajer, Salehi & Moradlou, 2016), and discriminant analysis (DA) (Fernandez et al., 2016; Haack et al., 2016; Silva et al., 2017) have been successfully used in studies from different fields of soil science. DA is mostly used to predict group discrimination based on observed predictors (Valaee, Ayoubi, Khormali, Lu, & Karimzadeh, 2016); for instance, it may be used for differentiating the weathering of soils developed from different rock types. We hypothesize that discriminant analysis may be a useful tool for revealing the contrasting granite types under diverse tropical climates.

Here, we studied the mineralogical properties and chemical composition of soils on different granite types using energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM) and a discriminant analysis approach to understand the relationship between soil geochemical signatures and the underlying granitic parent materials. We hypothesized that different granite types can be indicators of soil fertility from an agrogeological perspective and may also indicate which soil properties can be used as proxies for the presence of granites with contrasting compositions.

Material and methods

Study region

The study was carried out in the Borborema Province, Pernambuco state, northeast Brazil. This area comprises a mosaic of tectonic blocks, including a Paleoproterozoic basement and scattered Archean nuclei as well as Meso to Neoproterozoic supracrustal rocks with large intrusions of granites (Van Schmus et al., 2008). Neoproterozoic magmatism in the Borborema Province has produced voluminous S- and I-type granites. The petrographic and geochemical details of the I- and S-type granites found here have been described previously (Silva et al., 2016; Silva et al., 2017).

The study area covered three climatic settings within the Borborema Province: dry, sub-humid and humid zones (Figure 1). The dry zone has a semiarid climate (Bhs) with an annual precipitation of 500 mm and a mean annual temperature of 28°C. The sub-humid zone (Aw) has a transitional climate between the humid coastal area and the semiarid zone, presenting a longer dry season and lower precipitation (600-900 mm) compared to the humid zone. Finally, the humid zone has a typical tropical climate (Am) with a mean precipitation of 1,800 mm. In accordance with these contrasting climatic conditions, the vegetation demonstrates a clear zonation. A dry deciduous forest known as Caatinga covers the dry zone; semideciduous and primary evergreen forests (Atlantic rainforest) predominate in the sub-humid and humid zones, respectively (Nascimento, Oliveira, Ribeiro, & Melo, 2006).

Soil and Rock sampling

Samples of six soil profiles and their underlying rocks were taken from the three climatic zones. The sampling sites were chosen based on geological maps and confirmed on site (Figure 1). The sampling was carried out in relatively undisturbed environments to guarantee minimal anthropic influence and similar topographic conditions (gently sloping sites were prioritized). None of the diagnostic criteria for lithic discontinuity were in evidence in the soil profiles studied here (IUSS Working Group WRB, 2014), and hence, the soils developed directly from the underlying rocks.

Soil samples from all horizons were air-dried and sieved (< 2 mm) prior to analysis. Soil profiles derived from I-type granites were classified as eutric Regosols (dry and sub-humid zone) and hypereutric chromic lixisols (humid zone), whereas those developed from S-type granites were classified as eutric regosols (dry zone), dystric regosols (sub-humid zone) and dystric xanthic ferralsols (humid zone) according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). Fresh granite samples were collected from outcrops near the site of soil collection.

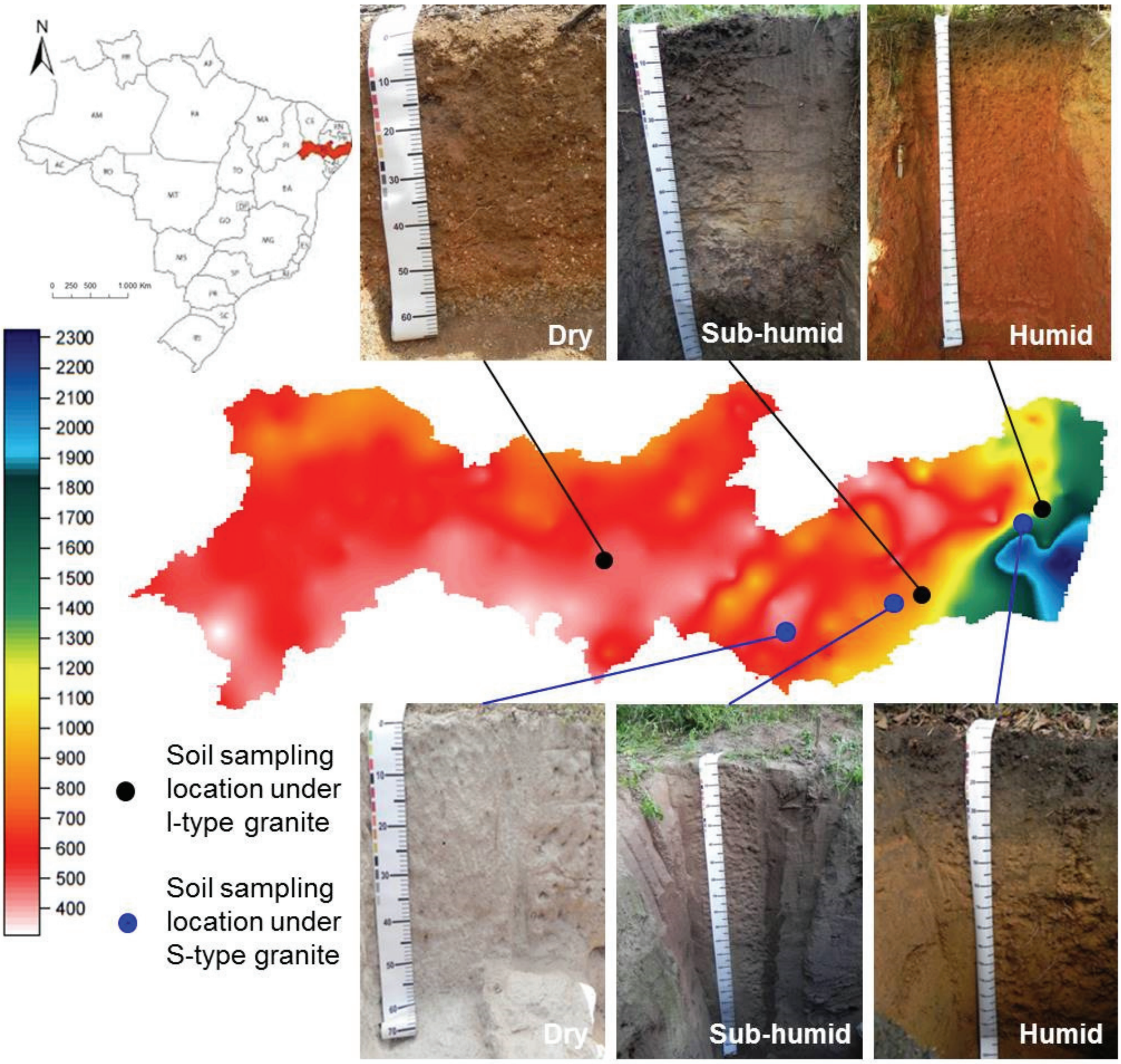

Figure 1. Location of the studied soil profiles over I-type and S-type granites in three contrasting climatic zones of Pernambuco State, Borborema Province, Northeast Brazil. Color in maps stands for precipitation rates.

Granite analyses

The I- and S-type granites and their modal mineralogical compositions were determined in the fresh rock samples taken *in situ*. A petrographic microscope was used for mineral identification, which was performed in polished thin sections prepared according to Murphy (1986).

After optical microscopy, rock thin sections were coated with a 20-nm gold layer (model Q150R - Quorum Technologies) for mineral identifications by a scanning electron microscope (SEM) (TESCAN, VEGA-3 LMU) at an accelerating voltage of 15 kV. Afterwards, SEM-based energy dispersive X-ray spectroscopy (EDS) (Oxford Instrument, model: 51-AD0007) was used to determine the elemental composition of the mineralogical assembly.

Soil analyses

Particle size distribution of the soil samples previously treated with 30% H_2O_2 was determined according to Gee and Or (2002) using Calgon for chemical dispersion. Values of pH were obtained in H_2O (1:2.5 soil: solution ratio), potential acidity ($H^+ + Al^{3+}$) was determined via the calcium acetate method (0.5 mol L^{-1}, pH 7.0), and total organic carbon (TOC) was measured according to Yeomans and Bremner (1988). To calculate the sum of the bases (SB), cation exchange capacity (CEC) and aluminum saturation, Ca, Mg, K and Na were determined. Potassium and Na^+ were extracted with Mehlich-1, while Ca^{2+}, Mg^{2+}, and Al^{3+} were extracted with 1 mol L^{-1} KCl. All elements were measured with optical emission spectroscopy (ICP-OES/Optima 7000, Perkin Elmer) using a dual observation mode (axial and radial) and a solid-state detector.

Weathering rate

The chemical index of alteration (CIA) was calculated according to Nesbitt and Young (1982):

$$CIA = [Al_2O_3 / (Al_2O_3 + Na_2O + CaO + k_2O)] \times 100.$$

For this calculation, the molecular proportions of the major elements (expressed as oxides) were determined by X-ray fluorescence spectrometry (XRF) (S8 TIGER ECO - WDXRF). Loss on ignition was determined at 1,000°C. The analysis quality was verified using an international geochemical standard from the National Institute of Standards and Technology (SRM 2709 San Joaquin soil, NIST, 2002). The recovery rates (%) were Al (106), Ca (105), Fe (100), K (98), Mg (96), and Na (72).

Statistical analysis

The data were assessed by discriminant analysis (DA). By simultaneously analyzing several variables, the DA assesses the differences among the groups by defining the independent variables that are most important to distinguish selected data sets. The groups were defined based on parent rocks (I- and S-type granites) and climate conditions (humid, sub-humid and dry zones). Exploratory data treatments based on DA identified the main factors determining the variability among soils with regard to parent material and climatic environment. All statistical analyses were performed with XLSTAT statistical software (version 2014.5.03).

Results and discussion

Granite types vs. soil characteristic

The mineralogical composition of I-type granites is summarized as follows: K-feldspar (60%) > quartz (9%) = plagioclase (9%) > biotite (8%) > amphibole (5%) > opaque minerals (4%) > allanite (2%) = apatite (2%) > titanite (1%). S-type granites, in turn, showed the following composition: K-feldspar (35%) > quartz (28%) > plagioclase (18%) > biotite (11%) > muscovite (5%) > opaque minerals (2%) > allanite (1%). These mineralogical compositions are in accordance with the chemical properties of I- and S-type granites reported by Chappell & White (2001). As a result of these differences, soils developed from I- and S-type granites had sharply contrasting characteristics (Tables 1 and 2).

Table 1. Selected chemical and physical characteristics of soil profiles derived from S-type granites in different climatic zones of Northeast Brazil.

Horizon/depth (cm)	TOC[a]	pH	CEC[b]	BS[c]	Sat. Al^{3+}[d]	Clay	Silt	Sand	CIA[e]
	(g kg^{-1})	(H_2O)	($cmol_c$ kg^{-1})	------- (%) -------		------- (g kg^{-1}) -------			(%)
Humid zone (348 m) – (Dystric Xanthic Ferralsols)									
A (0-9)	39.68	4.6	7.1	39	20.7	200	244	556	91
A (9-20)	14.83	4.3	5.8	28	44.0	200	263	547	94
AB (20-37)	9.01	4.2	4.6	26	56.5	200	361	439	95
BA (37-50)	7.00	4.1	4.3	37	39.8	230	385	385	95
Bw_1 (50-69)	4.23	4.2	3.0	38	51.1	230	364	406	96
Bw_2 (69-89)	3.87	4.1	2.7	33	55.8	220	350	430	95
Bw_3 (89-109)	3.64	4.1	2.5	33	55.5	200	362	438	95
Bw_4 (109-147)	5.53	4.2	2.5	38	52.3	230	348	422	96
Bw_5 (147-165)	4.05	4.1	2.6	38	51.8	250	365	385	96
Sub-humid zone (738 m) – (Dystric Regosols)									
A (0-16)	4.44	4.3	4.1	58	1.4	50	90	860	79
AC (16-34)	2.82	4.1	2.8	28	35.0	30	126	844	83
CA (34-56)	3.31	3.8	2.8	21	62.3	60	139	801	83
C_1 (56-93)	3.58	3.7	3.0	25	59.4	70	139	791	85
C_2 (93-111)	2.60	3.9	3.2	25	58.4	80	137	783	84
C_3 (111-136)	1.29	3.8	2.8	28	59.7	70	166	764	84
C_4 (136-152)	1.44	4.0	2.3	25	66.6	60	161	779	82
C_5 (152-195)	1.16	4.2	2.3	53	41.4	70	183	747	82
Cr (195-205)	-	-	-	-	-	-	-	-	72
Dry zone (389 m) – (Eutric Regosols)									
Ap (0-5)	4.57	6.0	2.8	88	0.0	40	51	909	58
CA (5-17)	3.18	5.3	2.2	75	8.2	50	80	870	61
C_1 (17-26)	1.98	5.2	2.2	70	16.0	50	97	853	62
C_2 (26-40)	2.62	4.8	2.4	74	14.6	50	113	837	62
C_3 (40-48)	1.77	5.2	2.4	81	7.0	40	120	840	61
Cr (48-59)	-	-	-	-	-	-	-	-	62

[a] Total organic carbon; [b] Cation exchange capacity; [c] Base saturation; [d] Aluminum saturation; [e] Chemical index of alteration.

Table 2. Selected chemical and physical characteristics of three soil profiles derived from I-type granites in different climatic zones of Northeast Brazil.

Horizon/depth (cm)	TOC[a]	pH	CEC[b]	BS[c]	Sat. Al^{3+}[d]	Clay	Silt	Sand	CIA[e]
	(g kg^{-1})	(H_2O)	(cmo_c kg^{-1})	--------- (%) ---------		------- (g kg^{-1}) -------			(%)
Humid zone (537 m) – (Hypereutric Chromic Lixisols)									
Ap (0-8)	59.58	5.5	8.5	63	0.5	150	379	471	90
AB (8-18)	58.43	5.0	7.2	56	1.4	170	383	447	91
BA (18-30)	11.97	4.7	5.5	56	4.7	180	414	406	93
Bt_1 (30-46)	6.37	4.8	4.6	59	3.5	250	440	310	94
Bt_2 (46-64)	5.72	5.2	4.2	64	0.0	300	507	193	97
Bt_3 (64-84)	4.19	5.0	4.2	62	1.9	310	506	184	98
Bt_4 (84-135)	1.50	5.0	4.0	65	1.9	300	522	178	98
BC (135-175)	3.66	5.0	3.8	65	0.0	260	569	171	98
C (175-195+)	3.07	4.8	3.6	64	10.6	270	558	172	98
Sub-humid zone (695 m) – (Eutric Regosols)									
A (0-11)	45.27	5.2	9.1	68	1.6	50	290	660	70
BA (11-17)	6.99	5.2	5.8	70	1.2	60	282	658	71
C_1 (17-46)	3.95	5.1	4.5	67	3.2	50	280	670	70
C_2 (46-70)	2.06	5.5	3.4	73	3.9	50	300	650	68
C_3 (70-78)	1.65	5.7	2.5	70	5.5	50	240	710	64
Cr_1 (78-148)	-	-	-	-	-	-	-	-	93
Cr_2 (148-185)	-	-	-	-	-	-	-	-	87
Cr_3 (185-200)	-	-	-	-	-	-	-	-	79
Dry zone (473 m) – (Eutric Regosols)									
A (0-3)	39.64	7.1	10.6	100	0.0	50	195	755	56
CA (3-9)	11.29	6.9	10.8	100	0.0	80	304	616	70
C_1 (9-17)	7.09	6.0	7.5	100	0.7	100	321	579	74
C_2 (17-27)	4.97	5.5	8.2	100	0.9	110	308	582	76
C_3 (27-39)	4.08	5.1	8.0	100	1.8	120	326	554	78
Cr_1 (39-53)	-	-	-	-	-	-	-	-	83
Cr_2 (53-63+)	-	-	-	-	-	-	-	-	75

[a] Total organic carbon; [b] Cation exchange capacity; [c] Base saturation; [d] Aluminum saturation; [e] Chemical index of alteration.

The higher proportion of weathering resistant minerals in S-type granites (i.e., quartz and muscovite) explains the higher sand contents in soils derived from S-type granites (Table 1) compared with the soils from I-type granite (Table 2) regardless of the climatic zones. TOC concentrations in soils may be related to clay contents (Table 2) — probably in response to the ability of clay minerals to stabilize and protect organic matter against mineralization (Schmidt et al., 2011; Lehmann & Kleber, 2015). This finding likely explains the accumulation of OC being higher in soils originating from I-type granites.

The granite types also markedly influenced the CEC and base saturation — characteristics that are linked to soil fertility. Overall, we found that I-type granites were associated with more fertile soils. Therefore, the rock composition might be used to define soil zones according to their cropping potential in an agrogeological perspective.

Corn and common beans are the main crops grown in the region, and their lime and fertilizer requirements are lower in soils developed from I-type than from S-type granites. Therefore, granite types along with data such as soil testing and mean annual rainfall can identify land areas homogeneous enough to be served by the same fertilizer recommendation. Such an approach can be used in soils that have developed under similar granite types worldwide (Zhao, Zhou, Li, & Wu, 2008; Canosa, Izard, & Fuente, 2012; Chappell, Bryant, & Wyborn, 2012; Guan et al., 2014; Foden, Sossi, & Wawryk, 2015; Robinson, Foden, & Collins, 2015).

I-type granites had mean CIA values that were higher than S-type granites (Tables 1 and 2). This finding is probably due to the higher concentration of more easily weathered minerals, such as apatite and amphibole, in the I-type granites. The higher proportion of accessory minerals in the soils that developed from I-type granites also explains their higher natural soil fertility (Table 2). Microscopic images of apatite, magnetite, zircon, and biotite as well as their chemical compositions by SEM/EDS (Figure 2) demonstrated that these minerals are among the main sources of plant nutrients along with amphibole (a mineral found only in I-type granites).

Discriminant analysis

The DA used chemical and physical data from soils (TOC, clay, silt, sand, CEC, BS, Al saturation, pH_{H2O} and CIA) as grouping variables. Soil samples derived from I-type granite — although well dispersed along the "*y*" axis (factor 2) — are mostly concentrated in the negative end of factor 1 compared to the soil samples from the S-type granite (Figure 3a). This pattern of data distribution is related to the higher values of TOC, clay, and an overall better fertility (higher BS, CEC, pH and lower Al saturation), which are also concentrated negatively along the "x" axis (factor 1) (Figure 3b).

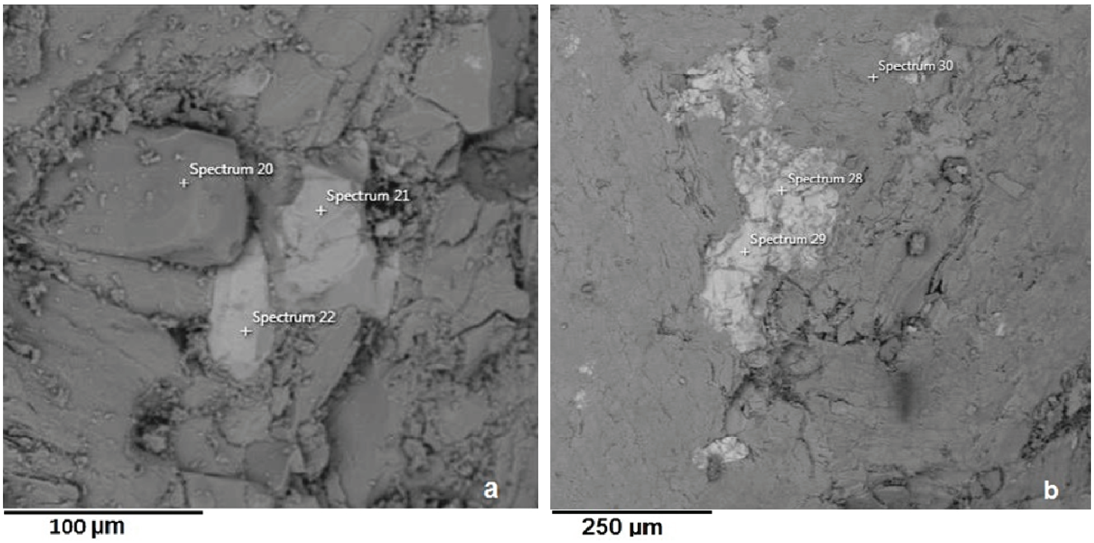

Figure 2. Scanning electron microscope (SEM) image captured from I-type granites and their respective elemental composition by energy dispersive X-ray spectrum (EDS). (a) Chemical composition of apatite (Spectrum 20: Ca – 67%, P – 29%, Fe – 1%, Si – 1%, Al – 1% K – 1%), magnetite (Spectrum 21: Fe – 98%, Si, Al, Ca – 1%), and zircon (Spectrum 22: Zr – 78%, Si – 20%, Fe – 2%). (b) Chemical composition of magnetite: spectrum 28 (Fe – 98%, Si, Al – 1%) and spectrum 29 (Fe – 98%, Si, Al – 1%); and biotite (Spectrum 30 Si – 33%, Fe – 25%, Al – 16%, K – 13%, Mg 11%, Ti – 2%).

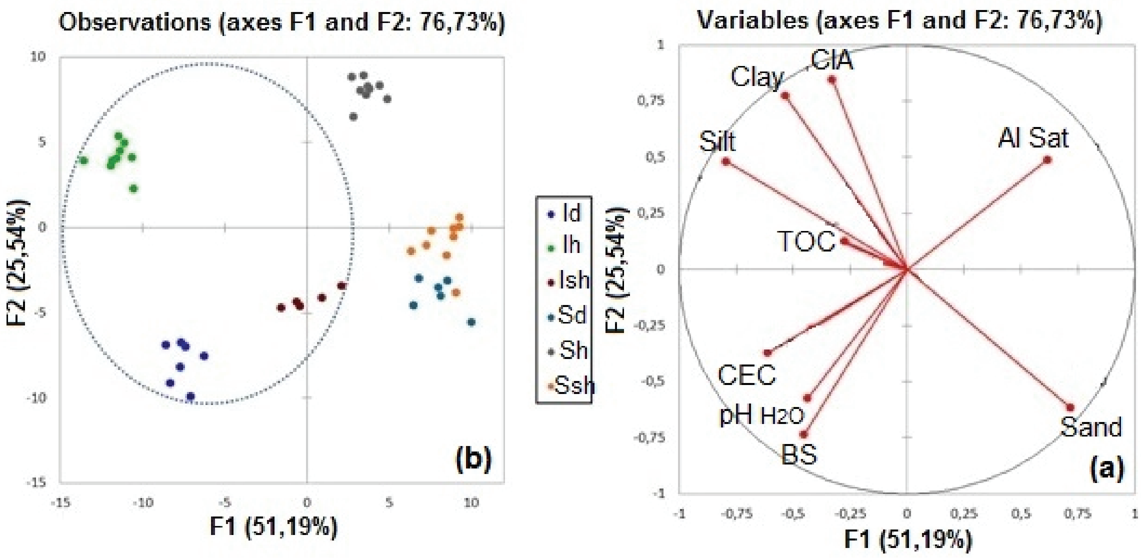

Figure 3. Discriminant analysis based on the chemical and physical characterization and weathering index (CIA) in (a), soils that developed from I- and S-type granites in Pernambuco State and (b), Northeast Brazil. I - I-type granite; S – S-type granite; d – dry zone; h – humid zone; sh – sub-humid zone.

The samples from soils that developed over S-type granites are mostly concentrated on the positive "*x*" axis (Figure 3a) in contrast to TOC and clay contents — a distribution pattern reflected by Al saturation and sand contents (Figure 3b). The grouping pattern indicates a contrast in weathering rates between soils developed from I- and S-types granites. These results can be mostly explained by the contrasting mineral composition of the parent rocks (Silva et al., 2017).

Soils formed from I-type granites showed a clear weathering gradient among the different climatic zones as evidenced by DA (Figure 3a). Data grouping showed the following increasing weathering degree: humid zone > sub-humid zone > dry zone. As indicated by factor 1 (Figure 3a), soil samples from humid zones were distributed positively along the "*y*" axis, whereas soil samples from sub-humid and dry zones (both granite types) were positioned negatively.

The distribution of the soil samples from the humid zone (Figure 3a) were clearly associated with the highest CIA values and the highest clay contents (Figure 3b). In contrast, soils from the sub-humid zone, and especially those from the dry zone, showed an opposite trend and remained distributed in the negative parts of both the "x" and "y" axes (factors 1 and 2, respectively) (Figure 3a). These samples were associated with higher CEC and BS values (Figure 3b), which indicates a more conservative environment.

The climate effects on weathering were less evident for soils that developed over S-type granites — especially for samples from the sub-humid and dry zones (Figure 3a). This inability to separate these two climatic zones by DA is a reflection of the higher amounts of highly resistant minerals in the S-type granites. This relationship governs the intensity of weathering more than the climate condition.

Conclusion

Soils originating from I-type granites presented higher chemical alteration than S-type derived soils. The mineralogical composition of the rocks likely explains why S-type granites carry a higher concentration of more stable minerals such as quartz and muscovite. The chemical composition of granites also influences soil fertility. Soils that developed from I-type granites showed a higher concentration of mineral nutrients than S-type-derived soils due to their overall lower concentrations of P, K, Ca, and Mg (feldspars, amphibole and apatite). I-type granites formed soils with higher clay contents and organic matter than soils originating from S-type granites. The integration of detailed mineralogical characterization of the granite types along with their chemical and physical analyses, using multivariate analysis can be an important approach in the understanding of the weathering process of granites across a climatic gradient.

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