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Geochemistry and Spatial Variability of Rare Earth Elements in Soils under Different Geological and Climate Patterns of the Brazilian Northeast

Cinthia Maria Cordeiro Atanázio Cruz Silva(1), Ronny Sobreira Barbosa(1), Clístenes Williams Araújo do Nascimento(2), Yuri Jacques Agra Bezerra da Silva(1)* and Ygor Jacques Agra Bezerra da Silva(2)

(1) Universidade Federal do Piauí, *Campus* Professora Cinobelina Elvas, Curso de Bacharelado em Engenharia Agronômica, Bom Jesus, Piauí, Brasil.
(2) Universidade Federal de Pernambuco, Departamento de Agronomia, Recife, Pernambuco, Brasil.

ABSTRACT: Growth in the agricultural and industrial sectors has increased the demand for rare earth elements (REEs) in the production of technological devices and fertilizers. Thus, the accumulation of these elements in the soil has become an environmental concern. Here, we aim to determine the natural contents of REEs in soils derived from different parent materials and under climatic conditions ranging from humid to semi-arid. We then evaluate the influence of major elements and soil properties on the geochemistry of REEs. The contents of REEs were determined using inductively coupled plasma optical emission spectroscopy. Major elements were determined by X-ray fluorescence spectrometry. The mean content of REEs in soils from Rio Grande do Norte (RN), Brazil, were in the followed order (mg kg^{-1}): Ce (40.4) > La (18.9) > Nd (15.8) > Pr (7.3) > Sm (3.0) > Gd (2.6) > Dy (1.0) > Er (0.7) > Yb (0.6) > Eu (0.5) = Tb (0.5) > Ho (0.3) > Lu (0.2). The parent material was the main factor that governed the geochemistry of the REEs in soils of RN. Higher levels of REEs were observed in soils derived from igneous and metamorphic rocks. In contrast, sedimentary rocks - except for the region formed from limestone - generated soils with lower contents of REEs in the state. In addition, soils developed from the same parent material and under different climatic conditions showed the same geochemical signatures for REEs in soils. These results confirm the small effect of climate on REE geochemistry in soils of RN and lead to the conclusion that the geochemical signature of REEs in these soils reflects the composition of the underlying parent material. The lack of significant correlation between $(La/Yb)_N$ ratio and the Chemical Alteration Index also confirms the low influence of climate on soil REE geochemistry. Among the major elements, Fe and Si had a greater influence on soil REE geochemistry. Higher REEs were seen in areas with more Fe and less Si. These REE levels were clearly controlled by the type of parent material. The Nd, Sm, Tb, Dy, Ho, Yb, and Er levels showed strong spatial dependence; this dependence was moderate for the Pr, La, Ce, Eu, Gd, and Lu levels. Spatial variability maps of REEs are particularly important to identify areas under environmental impact. Our results represent the most detailed study of the surface geochemistry of REEs in Brazilian soils and contribute to the scarce data available on these elements in Brazil.

Keywords: natural contents, lanthanides, geostatistics, factor analysis, soil quality.

*** Corresponding author:**
E-mail: yurijacques@ufpi.edu.br

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INTRODUCTION

Rare earth elements (REEs) are a group of fifteen chemical elements in the lanthanide series. These elements are divided into light rare earth elements (LREEs; La to Eu) and heavy rare earth elements (HREEs; Gd to Lu) based on the atomic number (Tyler, 2004; Hu et al., 2006a; Sadeghi et al., 2013; Davranche et al., 2016). Not all are technically "rare" - indeed, cerium is the 25th most abundant element in the Earth's crust, with contents similar to Cu and Zn (Tyler, 2004). Rare earth elements can be found in more than 270 primary and secondary minerals (Chakhmouradian and Wall, 2012; Jordens et al., 2013). They are mainly found in Fe and Al phosphates, carbonates, silicates, and oxides. Parent material and climate directly influence soil REE geochemistry (Zhang et al., 2001; Cidu et al., 2013; Silva et al., 2017). The intensity of weathering controls the transformation of minerals that act as sources of REEs in soils and several other environmental compartments.

The growth of the agricultural and industrial sectors has increased the demand for REEs in the production of technological devices (Strauch et al., 2008; Long et al., 2010; USEPA, 2012). Due to disposal of these materials at the end of their useful life, the accumulation of REEs in the soil is an environmental concern (Wang and Liang, 2016). Knowledge of the natural levels of REEs in soils is the first step in monitoring potentially contaminated areas. In addition, determination of these values deserves special attention because of the wide utility of these elements as tracers of soil erosion (Zhu et al., 2011; Wen et al., 2014), pedogenetic processes (Berger et al., 2014; Silva et al., 2017), and geochemical cycles (Viers et al., 2009).

Geochemical associations between major elements and REEs in different climatic conditions are important for understanding the behavior of REEs in soils (Laveuf et al., 2012). Some authors have observed a high correlation between REEs and Fe in tropical soils (Silva et al., 2016; Alfaro et al., 2018). This is logical because the process of weathering and crystallization of Fe oxides can release REEs.

Spatial variability of REEs represents the scale of change in geology and helps identify REE hotspots and their sources (Wang and Liang, 2016). This approach assists in observing the influence of climate and parent material on REE distribution. Spatial distribution of soil properties is often described (Aquino et al., 2015; Azevedo et al., 2015; Camargo et al., 2015; Shukla et al., 2016; Moraes et al., 2017). However, the spatial variability of REEs has rarely been shown. Spatial variability maps are particularly important for identifying areas subject to environmental impact - an essential step in establishing future environmental policies that affect human health and environmental protection. In this context, we aim to determine the natural levels (background) of REEs in soils derived from different parent materials and in climatic conditions ranging from humid to semi-arid; and to evaluate the influence of major elements and soil properties on the geochemistry of REEs. This study fills a gap in the scarce data on surface geochemistry of REEs in Brazilian soils.

MATERIALS AND METHODS

Study area and sample preparation

The study area covers the state of Rio Grande do Norte, Brazil, whose total area is 52,796.79 km². The sampling sites were selected based on the exploratory map of soil recognition (Brasil, 1968) and the geological framework of the state adapted from Medeiros et al. (2010). Soil and climate were considered for this sampling, and the soil samples included the most representative geomorphological, pedological, and geological compartments of the state.

Rio Grande do Norte can be divided into two major climatic environments. The semi-arid region covers a large part of the state's territory, with mean annual rainfall between 500-750 mm. The wetland is the second most dominant environment - it is located in the eastern portion of the state, with mean annual rainfall of 750-1,500 mm. The sub-humid region and semi-humid regions have mean annual rainfall of 800-1,200 and 600-800 mm, respectively. Mean annual air temperatures ranged from 26 to 27 °C.

The geology of the area is mostly pre-Cambrian (crystalline basement rocks), with Cretaceous units and Cenozoic sedimentary material (sediments of the Barreiras Group) (Figure 1) (Medeiros et al., 2010).

Different soil classes and source materials were represented by 104 composite soil samples (Figure 1). Each sample was formed from five simple samples. The samples were obtained with a stainless steel core sampling device from a layer of 0.00-0.20 m in places with minimal anthropogenic influence (geochemical background). Many definitions of geochemical background content are discussed in the literature (Tack et al., 1997; Matschullat et al., 2000; Reimann and Garrett, 2005; Dung et al., 2013). In the present study, geochemical background content is defined as the element content that has little to no influence from human activities and thus reflects natural processes (Matschullat et al., 2000). The soil samples were air dried, homogenized, and passed through a 2-mm sieve. A 5 cm^3 portion of soil was taken from each sample, macerated in an agate mortar, and passed through a stainless-steel sieve with 0.15 mm mesh openings (ABNT n° 100).

Physical and chemical characterization of the soil

Particle size analysis was performed according to Gee and Or (2002). Chemical characterization was performed according to Donagema et al. (2011). The pH was determined in water (1:2.5); Ca^{2+}, Mg^{2+}, and Al^{3+} were extracted with KCl 1.0 mol L^{-1} and titrated. Exchangeable K and Na were extracted with Mehlich-1 and measured by flame photometry. Potential acidity (H+Al) was determined by extraction with calcium acetate (0.5 mol L^{-1}) and titration. Organic carbon (OC) was determined via a modified Walkley-Black method (Silva et al., 1999). The values of the sum of bases (SB) and total cation exchange capacity (CEC) were

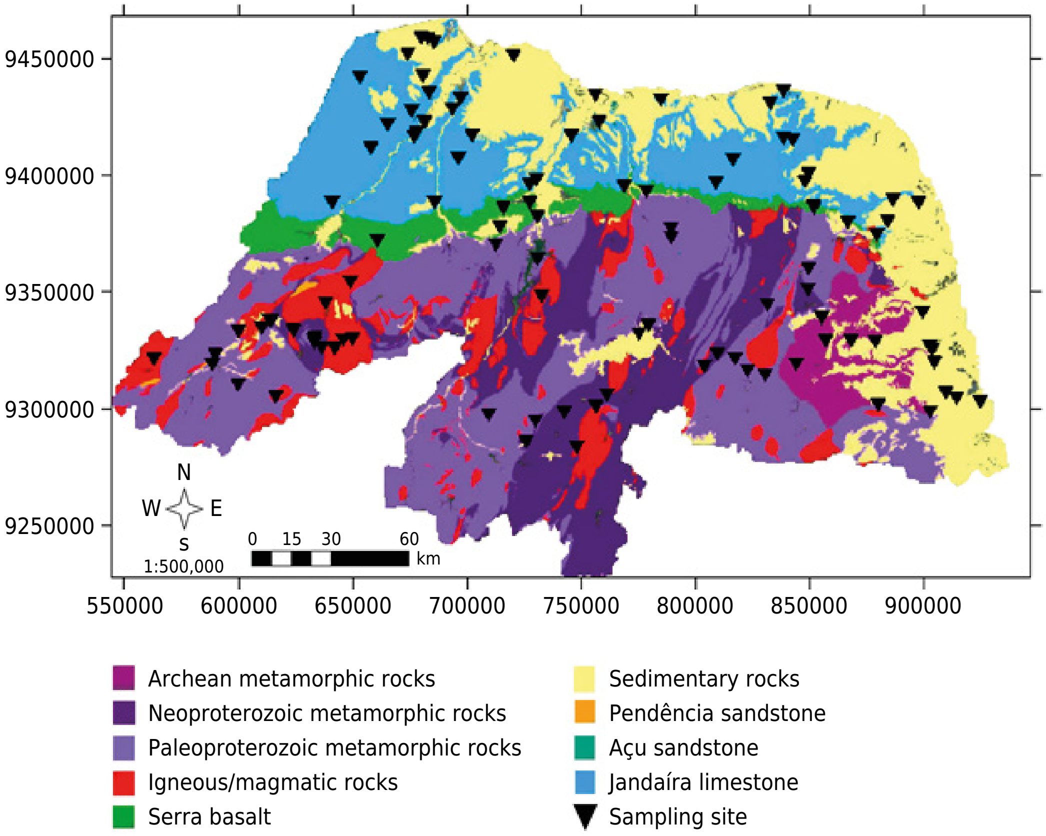

Figure 1. Simplified geological map of the state of Rio Grande do Norte, Brazil.

calculated from the results obtained from the sorptive complex. The soils exhibited wide variability in physical and chemical properties. In general, they are slightly acidic, with low organic carbon content (<1 %), and thus have low CEC. The sand content ranged from 8 to 97 g kg^{-1} and clay content from 2 to 64 g kg^{-1}.

Determination of rare earth elements and quality control

The extraction of REEs was performed according to methods from the United States Environmental Protection Agency (USEPA, 1998). This method extracts the REEs that are likely to become available over the medium- and long-term (Alloway, 2013). This extraction is considered to represent the ecologically or environmentally relevant fraction (REE contents in carbonates, sulfates, oxides, and less labile phases) (USEPA, 1998; Rauret et al., 1999; Rao et al., 2010; Loell et al., 2011). The method used a closed system (microwave oven) with 1 g of soil, 9 mL of HNO_3, and 3 mL of HCl (high purity acids - Merck, PA). The extracts were poured into 25 mL (NBR ISO/IEC certified) flasks, filled with ultrapure water (Millipore Direct-Q System), and filtered through slow filter paper (Macherey Nagel®). All analyses were performed in duplicate.

For control and data quality, blank samples and international SRM 2709 (San Joaquin Soil certification sample; NIST, 2002) were analyzed during each series of digestions. The concentrations of the REEs were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES/Optima DV7000, Perkin Elmer) using a cyclonic chamber system. The quality of the analysis was confirmed via the recovery rates of the REEs obtained from the SRM 2709 sample; rates were over 80 %.

Determination of major elements and calculation of CIA

The major elements (TiO_2, Al_2O_3, SiO_2, SO_3, Fe_2O_3, MgO, CaO, Cr_2O_3, MnO, Na_2O, K_2O, SrO, ZrO_2, BaO, and P_2O_5) were determined by X-ray fluorescence spectrometry with wavelength energy dispersion (S8 TIGER ECO - WDXRF-1KW). The sample was prepared via a hydraulic press at 25 tons. The fire loss was determined at 1000 °C. The quality of the data was verified by analyzing the certified sample SRM 2709 (NIST, 2002). The recovery rates of the major elements (%) decreased in the following order: P (114) > Al (106) > Ca (105) > Ti (101) > Fe (100) > K (98) > Mg (96) > Si (89) > Mn (86) > Na (80). The chemical alteration index (CIA) was calculated following the methodology of Nesbitt and Young (1982) (Equation 1):

$$CIA = [Al_2O_3 / (Al_2O_3 + Na_2O + CaO + K_2O)] \times 100 \qquad \text{Eq. 1}$$

Rare earth elements in the soils were normalized to the upper continental crust (UCC - La: 30; Ce: 64; Pr: 7.1; Nd: 26; Sm: 4.5; Eu: 0.88; Gd: 8; Tb: 0.64; Dy: 3.5; Ho: 0.8; Er: 2.3; Tm: 0.33; Yb: 2.2; Lu: 0.32 mg kg^{-1}) (Taylor and McLennan, 1985). Standardization was the first step in determining whether depletion or enrichment occurred relative to reference material. It also facilitated comparison of the REE content results with soils from other locations; normalization with the upper continental crust is common (Paye et al., 2016; Censi et al., 2017; Silva et al., 2017). Fractionation between the LREEs and HREEs $(La/Yb)_N$ was quantified. Specifically, Ce $[(Ce_N/(La_N \times Pr_N)^{0.5}]$ and Eu $[(Eu_N/(Sm_N \times Gd_N)^{0.5}]$ anomalies were calculated according to Compton et al. (2003) - values over 1 indicate enrichment relative to UCC.

Spatial distribution of REEs

The spatial dependence of the variables under study and their spatial distribution were obtained by geostatistical modeling (Vieira, 2000). The assumptions of stationarity in the intrinsic hypothesis were considered by Gamma Design Software 7.0 - GS + (Robertson, 1998). Adjustments were made via simple experimental semivariograms selecting the spherical, exponential, or Gaussian models and then determining the effect of nugget (C0), threshold (C0 + C1), structural variance (C1), and range. This selection used the smallest value of the sum of the squares of the residuals (SSR), followed by the highest value of the determination coefficient (R^2), and the highest value of the degree of spatial dependence (DSD).

The DSD was calculated according to the proposal of Cambardella et al. (1994) [C0 / (C0 + C1) × 100]. A nugget effect less than or equal to 25 % of the plateau was considered strong. The value was considered moderate when it was from 25 to 75 % and weak when greater than 75 %. The kriging algorithm was used here via Surfer 8.0 software for map manipulation.

Statistical analysis

The results were evaluated via descriptive statistics, Pearson correlation, regression analysis, and factorial analysis (FA). Factorial analysis was applied to assess REE behavior in soils derived from different geological patterns. As variables with difference in data magnitude and measurement scales were considered, a correlation matrix was applied to standardize each variable (Webster, 2001) and only eigenvalues greater than one were selected. This analysis converted the original group of variables, Z_1, Z_2,..., Z_n, into a new group of variables, Y_1, Y_2,...., Y_n, with equal dimensions, but uncorrelated. These new groups represent linear combination of the original variables, with the aim of explaining the maximum total variability associated with these independent variables (Manly, 2008). Varimax rotation was used to extract the most relevant factors and exclude variables with little or no influence on REEs content in soils (Kaiser, 1958; van den Boogaart and Tolosana-Delgado, 2013). Linear regression analyses between $(La/Yb)_N$ ratios and CIA values were tested to evaluate how fractionation is connected with weathering intensity.

RESULTS AND DISCUSSION

Natural content and reference values of REEs in RN soils

The mean REE contents in the soils was in the followed order: Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Eu = Tb > Ho > Lu (Table 1). The REE contents decreased with increasing atomic number according to the Oddo-Harkins rule (Laveuf and Cornu, 2009): Ce > Nd/La > Y > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu. The LREEs comprise 93 % of the total REEs in the soils, with Ce being the most abundant element. The contents of LREEs were similar to the contents found in soils from Pernambuco (Silva et al., 2016). However, the values were lower than those observed for the soils of China (Wei et al., 1991) and the

Table 1. Mean contents of rare earth elements (REEs) in the soils of Rio Grande do Norte, Brazil, compared to data from Pernambuco, Brazil, other countries, and the Earth's crust

REEs	RN	PE(2)	Cuba(3)	China(4)	Crust(5)
La (mg kg^{-1})	18.9	20.8	15.2	37.4	35.0
Ce (mg kg^{-1})	40.4	43.5	24.2	64.7	66.0
Pr (mg kg^{-1})	7.3	9.6	5.0	6.7	9.1
Nd (mg kg^{-1})	15.8	17.7	17.1	25.1	40.0
Sm (mg kg^{-1})	3.0	3.4	4.4	4.9	7.0
Eu (mg kg^{-1})	0.5	0.6	0.03	1.0	2.1
Gd (mg kg^{-1})	2.6	2.3	0.2	4.4	6.1
Yb (mg kg^{-1})	0.6	0.7	1.9	2.3	3.1
Lu (mg kg^{-1})	0.2	0.1	0.8	0.4	0.8
Dy (mg kg^{-1})	1.0	0.9	1.3	3.9	4.5
Er (mg kg^{-1})	0.7	0.6	2.4	2.4	3.5
Ho (mg kg^{-1})	0.3	0.2	0.6	0.8	1.3
Tb (mg kg^{-1})	0.5	0.5	1.2	0.6	1.2
∑LREEs	86.0	95.6	65.9	139.8	159.2
∑HREEs	5.9	5.2	8.2	14.8	20.5
∑REEs	91.9	100.8	74.2	154.6	179.7
∑LREEs/HREEs	14.5	18.3	8.0	9.4	7.8

(1) The extraction of REEs was performed according to USEPA (1998). (2) Silva et al. (2016). (3) Alfaro et al. (2017). (4) Wei et al. (1991). (5) Tyler and Olsson (2002).

continental crust (Tyler and Olsson, 2002). The HREE levels were half of those observed in China. Linear regression analyses between the $(La/Yb)_N$ ratio and CIA value ($r^2 = 0.012$; n =104; $p<0.26$) evidenced the low influence of climate on REE geochemistry in soils of RN. Thus, the type of parent material is the main factor that governs these differences.

To generate more information about the effect of geological settings on REE geochemistry in soils, results were organized according to the type of parent material (Figure 2a). Clearly, the REE contents in soils varied systematically according to the different geological units, decreasing in the following order: igneous units > limestone units > metamorphic units > clastic sediments (Figure 2a). The REE contents in soil normalized to UCC had a similar distribution pattern (Figure 2b). These findings demonstrate that, regardless of climatic conditions, the parent material factor highly influences REE geochemistry in soils. Several authors have observed that large variations in REE contents in soils are highly dependent on the types of parent material they are derived from (Hu et al., 2006b; Silva et al., 2017; Alfaro et al., 2018).

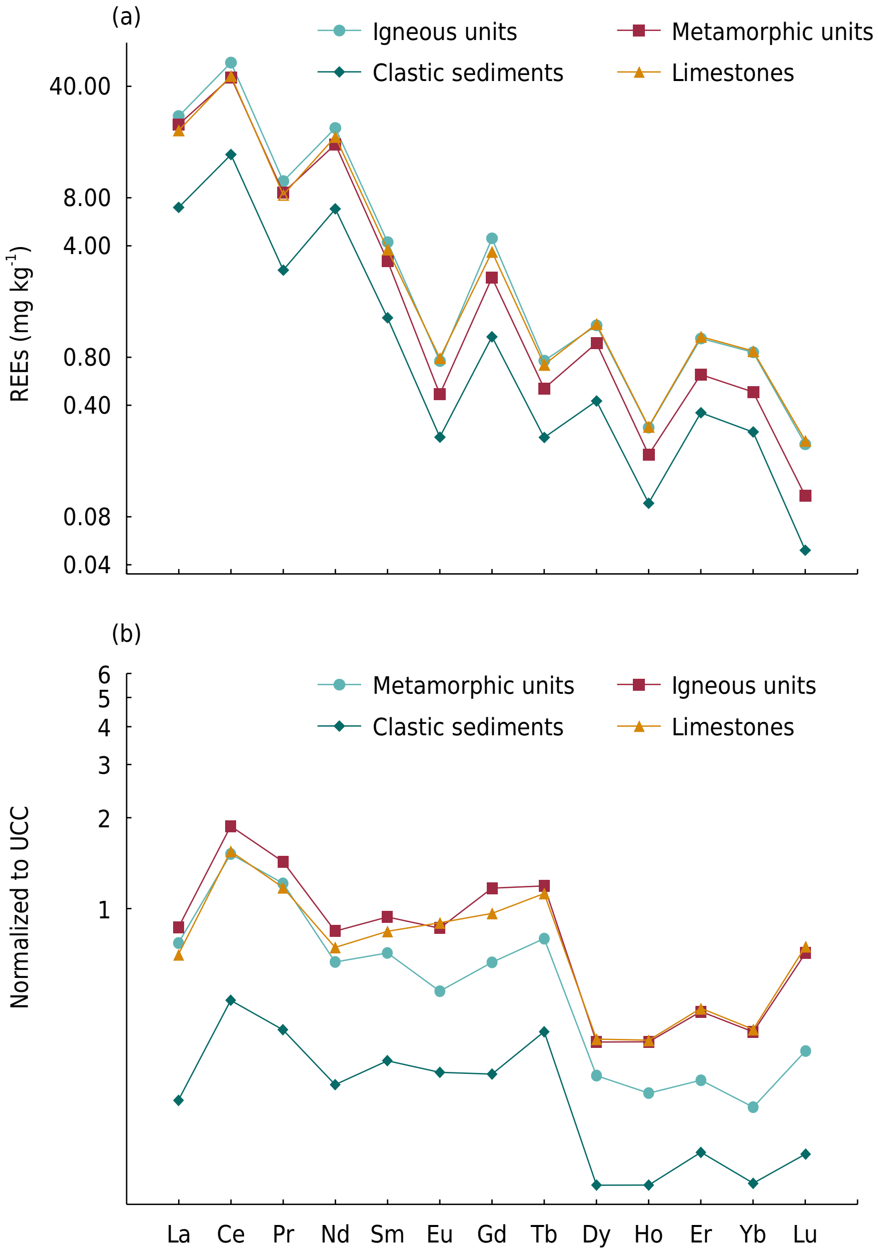

Figure 2. Rare earth elements in soils derived from different parent materials of the state of Rio Grande do Norte, Northeast Brazil. Non-normalized data (a). Data normalized to UCC (b).

Soils developed from different parent materials that formed under the same climatic condition (sub-humid zone) exhibited different geochemical signatures of LREE and HREE in soils (Figures 3a and 3b). The LREE and HREE contents in soils of this climatic zone reduced in the following order: igneous units > metamorphic units > clastic sediments (Figures 3a and 3b). There are no soils derived from limestone in the sub-humid zone. The similar distribution pattern of REEs observed in figures 2 and 3 also indicate that the geological unit is the main potential factor that governs REE dynamics in soils of RN.

In addition, soils derived from metamorphic units along a climosequence (sub-humid and semi-arid zones) had similar REE contents (Figure 4). This finding confirms the small effect of climate on REE geochemistry in soils of RN and leads to the conclusion that the geochemical signature of REEs in these soils largely reflects the composition of the underlying parent material.

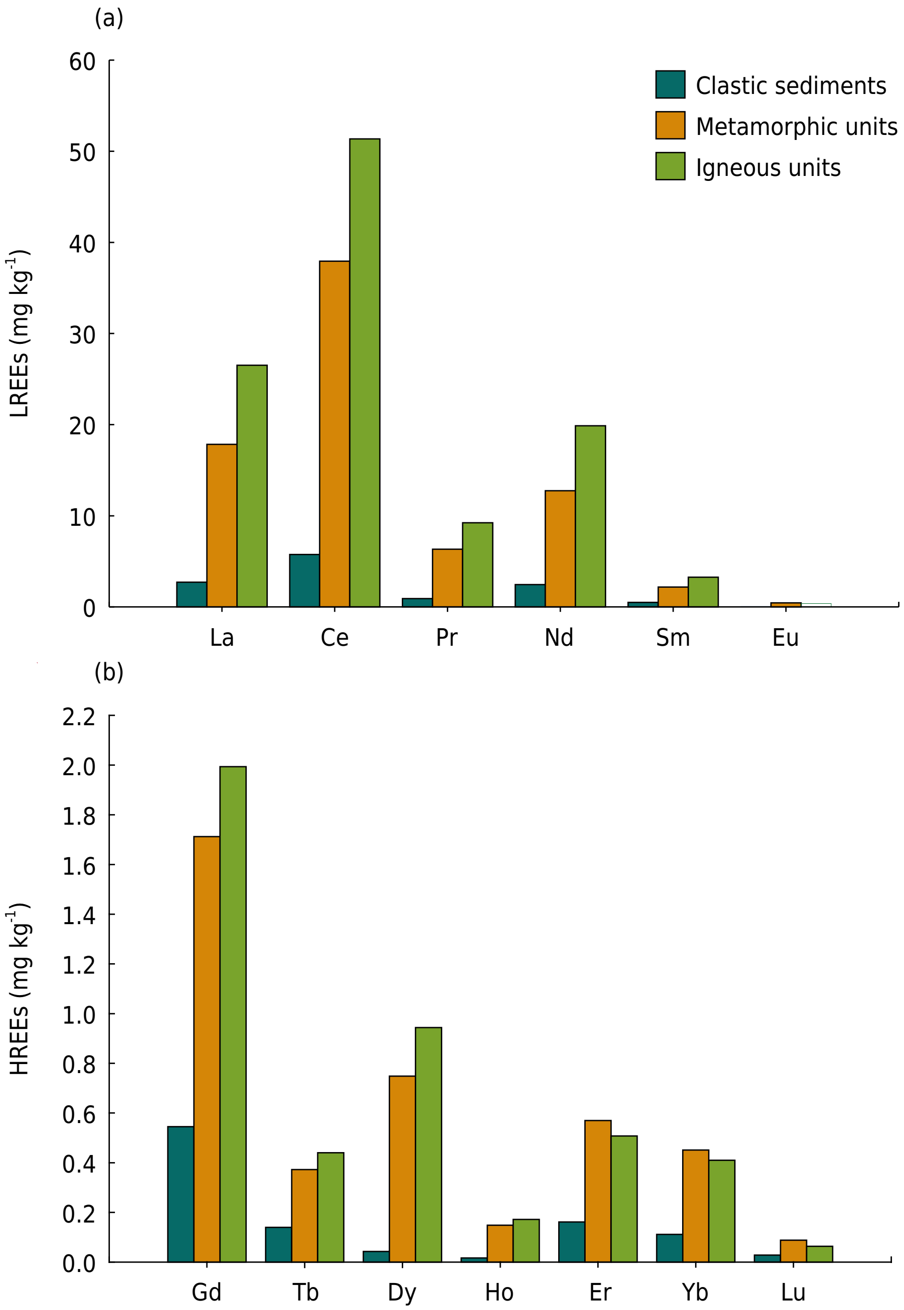

Figure 3. Light rare earth elements in soils derived from different parent materials in the sub-humid zone of the state of Rio Grande do Norte, Northeast Brazil (a). Heavy rare earth elements in soils derived from different parent materials in the sub-humid zone of the state of Rio Grande do Norte, Northeast Brazil (b).

The higher enrichment of LREEs was quantified via the $(La/Yb)_N$ and ΣLREEs/ΣHREEs ratios (2.36 and 14.5, respectively). The $(La/Yb)_N$ ratios, greater than one, suggest magma evolution occurred through crystal fractionation (Bolarinwa and Bute, 2015). This process can explain the higher occurrence of LREEs in the parent material. The enrichment of LREEs may also be associated with their more limited soil mobility (Laveuf and Cornu, 2009). The HREEs form more stable complexes with soil organic matter, facilitating their mobilization in soil (Henderson, 1984; Sonke, 2006); however, this effect was not observed in our data. Silva et al. (2017) studied the influence of the mineralogy of type I and S granites on the geochemistry of REEs in rocks and soils along a climosequence in Brazil. They saw no relationship between organic carbon content and REEs in soils.

Although soils under tropical and subtropical conditions commonly exhibit depletion of HREEs with increased weathering intensity (Laveuf and Cornu, 2009; Cao et al., 2016; Silva et al., 2017), the lack of significant correlation between HREE contents and CIA values (Table 2) indicates the small effect of weathering intensity on depletion of HREEs in soils. The lack of significant correlation among $(La/Yb)_N$ ratios and CIA values (Table 2) also confirms the small influence of climate on REE fractionation in soils.

Approximately 90 % of the samples had a negative Ce anomaly (0.64-0.98), indicating slight depletion of this element on the soil surface. Regardless of the parent material, in general, the Eu anomaly was slightly negative or absent in soils, with an average value of 0.99.

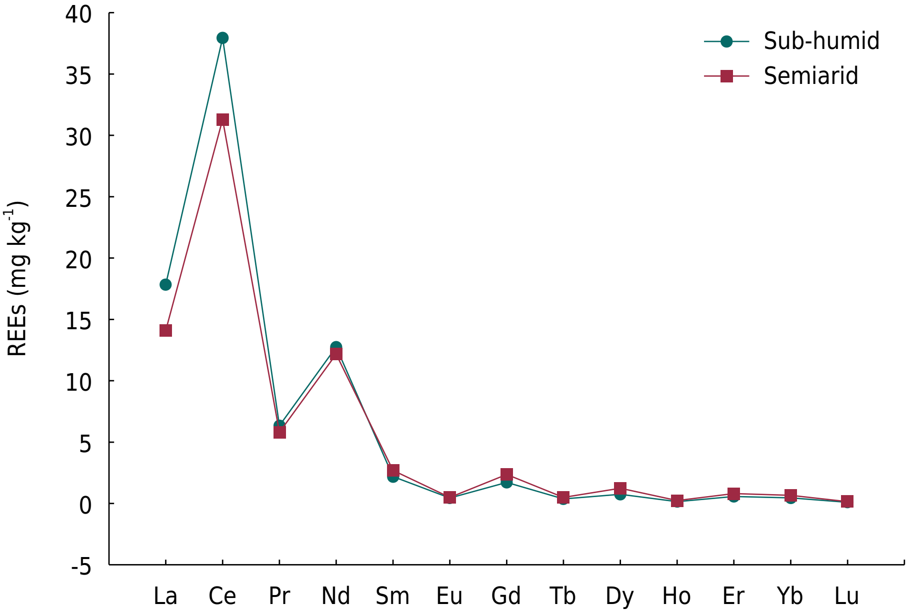

Figure 4. Rare earth elements in soils derived from metamorphic rocks across a climosequence (sub-humid and semi-arid zones) in the state of Rio Grande do Norte, Northeast Brazil.

Table 2. Pearson correlation coefficients among ∑HREE, ∑LREE, ∑REE, and CIA values in soils developed from different geological settings of Rio Grande do Norte, Brazil (n = 104 soil samples)

Variables	∑HREE	∑LREE	∑REE	CIA	$(La/Yb)_N$
∑HREE	1.00				
∑LREE	0.84*	1.00			
∑REE	0.86*	0.99*	1.00		
CIA	-0.25	-0.26	-0.26	1.00	
$(La/Yb)_N$	-0.24	0.03	0.01	-0.11	1.00

* Correlation is significant at the 0.01 level.

Influence of the major elements and the physical and chemical properties of the soil in the distribution of REEs

The mean content of the major elements in the soils were in the following order (%): Si > Al > Fe > K > Ca > Na > Ti > Mg > Zr > P > Ba > S > Mn > Cr = Sr (Table 3). The CIA ranged from 36.4 to 99.2 %, with an average value of 78.13 %, which might imply high proportions of feldspars in some samples. This confirms the low/intermediate/advanced intensity of soil weathering. This wide difference in the intensity of weathering and geological contexts (Figure 1) confirms that the dynamics of elements in the soil are more strongly influenced by the parent material. The negative correlation of the CIA with the larger and more mobile elements CaO (-0.67), Na_2O (-0.65), K_2O (-0.75), and BaO (-0.66) indicates leaching of these elements with increasing weathering intensity. This is mainly seen in coastal and sub-humid regions (Figure 8).

The moderate to high correlations facilitate factorial analysis (Table 4) to verify the influence of the major elements and the soil physical and chemical properties as a function of REE distribution. The light and heavy rare earth elements had a high positive correlation (0.69-0.99; $p<0.01$); for the HREEs, this ranged from 0.75 to 0.99 ($p<0.01$). High positive correlation was also observed between the LREEs and HREEs (0.71-0.98; $p<0.01$). The sand and clay fraction were inversely related and directly correlated with the REEs. Organic carbon and pH had no correlation with the REEs. Iron had the highest positive and Si had the highest negative correlation with REEs. The more mobile elements, such as Ca, Na, K, and Ba, had a negative correlation with the CIA weathering index. The spatial distribution of CIA and Ca + Na_2O + K_2O + BaO is shown in figure 5.

Table 3. Mean, minimum, maximum, and standard deviation for the major elements in Rio Grande do Norte soils

Major elements	Min	Max	Mean	SD
	%			
SiO_2	27.46	93.60	60.42	12.30
Al_2O_3	3.09	33.30	17.99	5.07
Fe_2O_3	0.44	18.50	4.89	3.14
MnO	0.01	0.30	0.07	0.06
CaO	0.06	7.57	1.47	1.52
MgO	0.08	4.34	1.02	0.94
Na_2O	0.08	13.50	1.35	1.75
K_2O	0.06	9.25	3.03	2.28
P_2O_5	0.05	1.73	0.19	0.23
TiO_2	0.15	10.80	1.21	1.11
ZrO_2	0.03	2.86	0.25	0.29
Cr_2O_3	0.01	0.09	0.04	0.02
SrO	0.01	0.17	0.04	0.03
BaO	0.04	0.40	0.17	0.08
SO_3	0.03	1.78	0.15	0.22

SD = standard deviation. The major elements were determined by X-ray fluorescence spectrometry with wavelength energy dispersion.

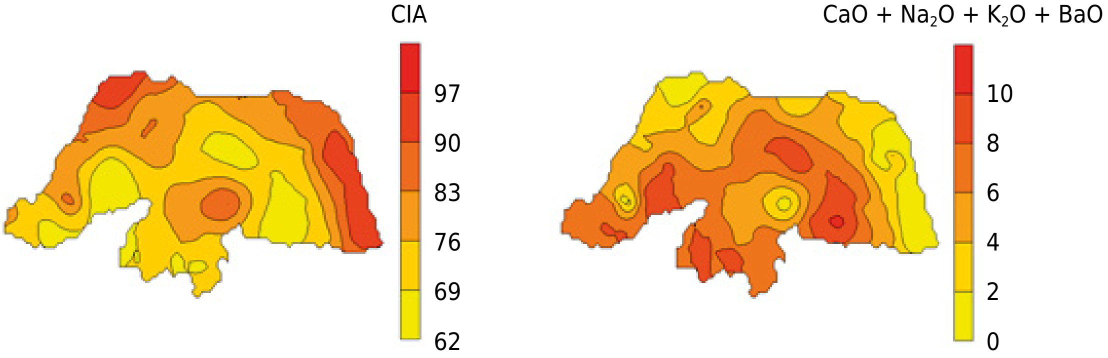

Figure 5. Spatial distribution of the chemical change index (CIA) and major elements in soils from Rio Grande do Norte, Brazil.

Factorial analysis helped to evaluate the influence of the major elements as well as the physical and chemical properties of the soil as a function of REE. Variables with little or no contribution (Al_2O_3, MgO, P_2O_5, TiO_2, ZrO_2, Cr_2O_3, SrO, SO_3, OC, and pH) were ruled out (Table 4). The first two factors had eigenvalues greater than one (F1 = 16.95 and F2 = 2.96) and explained approximately 74 % of the REE variation in soils.

The F1 was positively correlated with light and heavy REEs (0.84-0.98), sum of LREE (0.90), sum of HREE (0.97), sum of REE (0.91), Fe_2O_3 (0.74), MnO (0.60), clay (0.71), and CEC (0.62). It was negatively correlated with SiO_2 (-0.72) and sand (-0.72). The F2 was positively correlated with CaO (0.65), Na_2O (0.65), K_2O (0.73), and BaO (0.77), and negatively correlated with the CIA weathering index (-0.95). This indicates that higher weathering results in greater removal of more mobile cations. Soil pH and OC did not influence the content of surface REE. However, other studies have demonstrated an influence of OC and pH on the REEs content (Silva et al., 2016; Vermeire et al., 2016). This suggests that the chemical composition of the organic matter and the interaction of the chemical compartments with the REEs should be considered in future studies involving the geochemistry of these elements in soils. The effect of the clay content overlaps with the effect of the organic carbon.

Table 4. Factorial analysis of rare earth elements, major elements, and physical and chemical properties of soil

REEs	F1	F2
La	**0.84**	0.18
Ce	**0.88**	0.19
Pr	**0.89**	0.17
Nd	**0.94**	0.14
Sm	**0.97**	0.12
Eu	**0.95**	0.05
∑LREE	**0.90**	0.18
Gd	**0.92**	0.17
Tb	**0.98**	0.09
Dy	**0.91**	0.10
Ho	**0.94**	0.05
Er	**0.96**	0.02
Yb	**0.95**	0.01
Lu	**0.88**	-0.03
∑HREE	**0.97**	0.10
∑REE	**0.91**	0.17
SiO_2	**-0.72**	-0.21
Fe_2O_3	**0.74**	0.10
MnO	**0.60**	0.16
CaO	0.28	**0.65**
Na_2O	0.11	**0.65**
K_2O	0.10	**0.73**
BaO	0.01	**0.77**
CIA	-0.14	**-0.95**
Sand	**-0.72**	0.07
Clay	**0.71**	-0.24
CEC	**0.62**	0.13
Eigenvalues	16.95	2.96
EV (%)	62.77	10.96

EV = explained variance. Bold means significant values.

Distribution of rare earth elements in soils

The La, Nd, Sm, Tb, Dy, Ho, Yb, and Er had strong spatial dependence (Table 5), indicating that the sampling distance could provide data variance (Carvalho et al., 2011). In addition, the values of parameters “a” and “b” confirmed the precision of the adjusted semivariograms.

All LREEs had a similar distribution (Figure 6). However, lower contents were observed in soils derived from sedimentary rocks (Figure 1), except for the region formed by limestone. Higher contents were observed in soils composed of igneous and metamorphic rocks because this type of source material may contain a larger stock of REEs (Hu et al., 2006a). Although the climate is similar in the extremes of RN, there are LREE “hotspots” that show different behavior. This can explain why the source material is the main factor impacting REE contents.

Except for Gd, the HREEs had similar spatial distributions (Figure 7). The HREEs had lower contents in soils than the LREEs (Figure 8). This was expected because the HREEs have lower contents in the parent material (Henderson, 1984; Cantrell and Byrne, 1987; Hu et al., 2006a).

The spatial variability of REEs represents the scale of change in the geology and help identify the REE hotspots and their sources (Wang and Liang, 2016). This approach helps to observe the influence of climate and parent material on REE distribution (Silva et al., 2017). The spatial distribution of several soil properties is often described (Aquino et al., 2015; Azevedo et al., 2015; Camargo et al., 2015; Shukla et al., 2016; Moraes et al., 2017). However, the spatial variability of REEs has seldom been shown. These maps are particularly important to identify areas subject to environmental impact - an essential step in establishing future environmental policies that affect human health and environmental protection.

Table 5. Estimated models and parameters of the semivariograms of rare earth elements (REEs), iron (Fe_2O_3), clay, and CEC

Variables	Model	C_0	$C_0 + C$	DSD	ESD	Range	R^2	CRVC	
								a	b
				%		m			
La	Exponential	0.19	2.61	7	S	38100	0.58	5.77	0.71
Ce	Spherical	1.84	5.83	32	M	42700	0.66	10.65	0.78
Pr	Spherical	0.39	1.16	34	M	41300	0.67	1.95	0.79
Nd	Exponential	0.38	2.29	16	S	43800	0.58	2.98	0.88
Sm	Exponential	0.04	0.56	7	S	26700	0.61	0.50	0.95
Eu	Spherical	0.03	0.09	35	M	48000	0.66	0.14	0.78
Gd	Spherical	0.22	0.60	36	M	46300	0.81	0.88	0.77
Tb	Exponential	0.01	0.10	10	S	32400	0.73	0.12	0.87
Dy	Exponential	0.01	0.20	5	S	33000	0.60	0.32	0.74
Ho	Gaussian	0.01	0.06	11	S	17666	0.72	0.08	0.74
Er	Exponential	0.01	0.12	12	S	35100	0.76	0.19	0.79
Yb	Exponential	0.01	0.13	8	S	33300	0.77	0.10	0.96
Lu	Spherical	0.01	0.04	31	M	50400	0.84	0.05	0.79
LREEs	Spherical	3.16	12.49	25	S	40900	0.72	21.60	0.79
HREEs	Exponential	3.02	25.38	12	S	32700	0.73	0.79	0.86
REEs	Spherical	4.49	12.41	36	M	49200	0.61	21.00	0.80
Fe_2O_3	Exponential	2.39	6.52	37	M	61200	0.77	1.24	0.72
Clay	Spherical	0.98	2.77	35	M	47800	0.59	1.17	1

C_0 = nugget effect; C_0 + C1 = still; R^2 = determination coefficient; DSD [(C_0/C_0 + C) × 100] = degree of spatial dependence; ESD = evaluation of spatial dependence assessment; CRVC = cross-validated regression coefficient; a = intercept; b = angular coefficient; M = medium dependence; S = strong dependence.

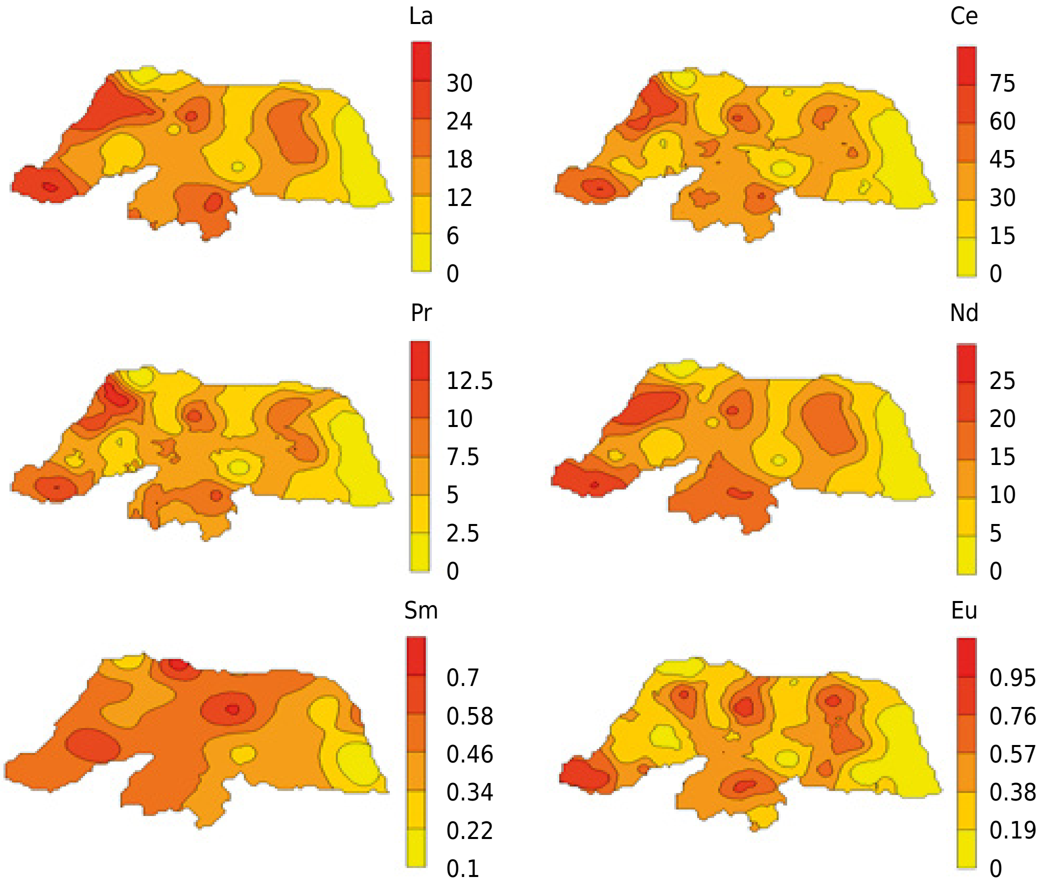

Figure 6. Spatial distribution of LREEs (mg kg^{-1}) in soils from Rio Grande do Norte, Brazil.

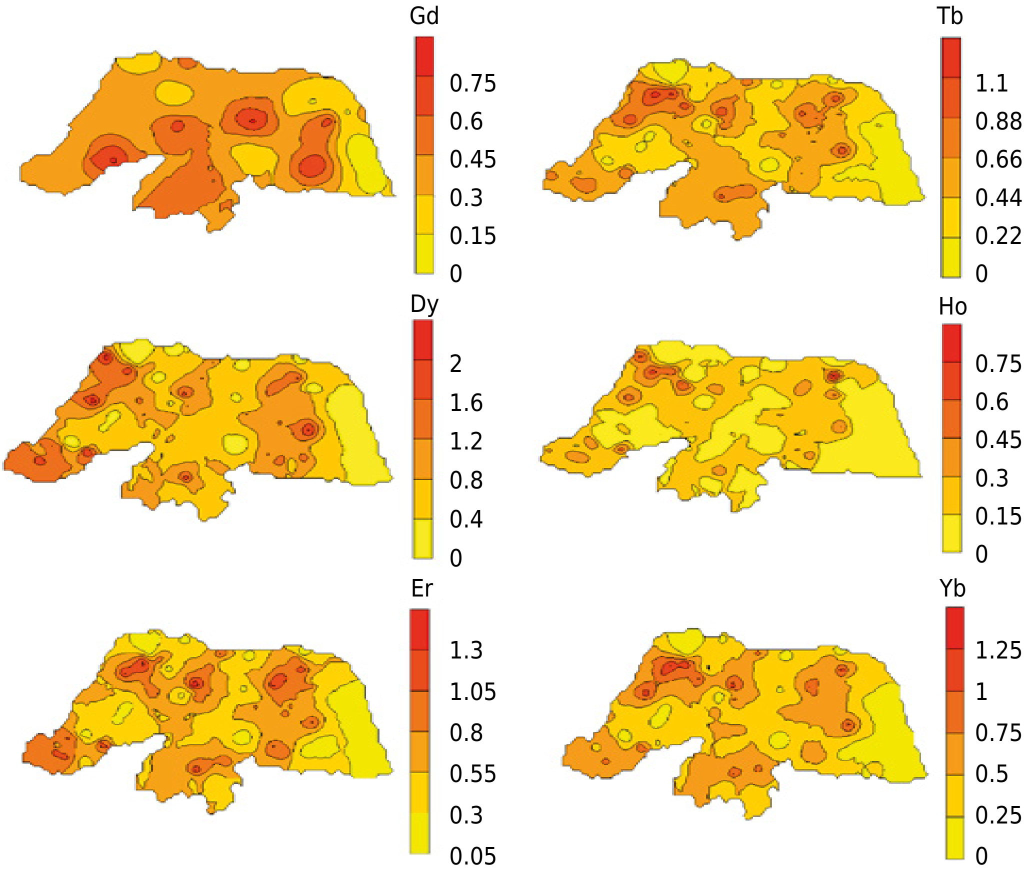

Figure 7. Spatial distribution of HREEs (mg kg^{-1}) in soils from Rio Grande do Norte, Brazil.

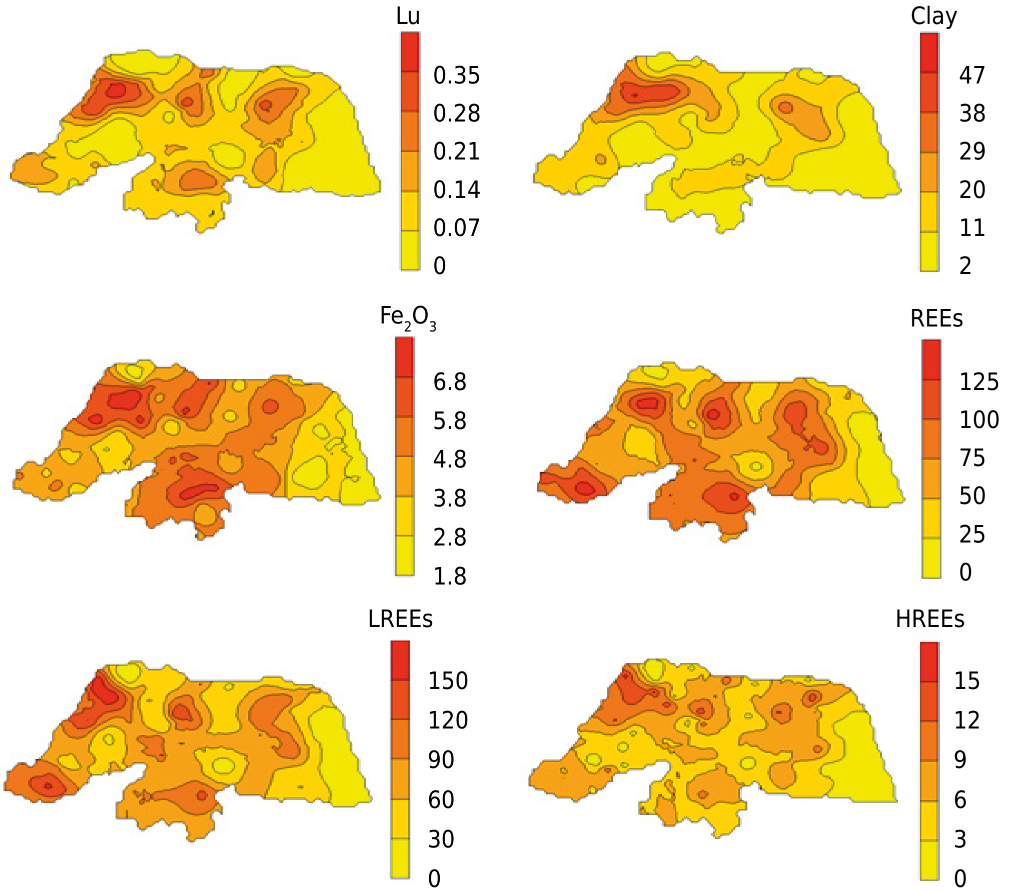

Figure 8. Spatial distribution of clay (%), Fe_2O_3 (%), lutetium, REEs, LREEs, and HREEs in mg kg^{-1}.

CONCLUSION

The parent material was the main factor that governed the geochemistry of REEs in soils of the state of RN, Brazil. Regardless of climatic conditions, the REE contents in soils varied according to the different geological units, decreasing in the following order: igneous units > limestone units > metamorphic units > clastic sediments. In addition, soils developed from the same parent material under different climatic conditions showed the same geochemical signatures of REEs in soils. These results confirm the small effect of the climate on REE geochemistry in soils of RN and lead to the conclusion that the geochemical signature of REEs in these soils largely reflects the composition of the underlying parent material. The lack of significant correlation between the $(La/Yb)_N$ ratio and CIA value also confirms the small influence of climate on soil REE geochemistry. The La, Nd, Sm, Tb, Dy, Ho, Yb, and Er had strong spatial dependence; this dependence was moderate for Pr, Ce, Eu, Gd, and Lu. Spatial variability maps of REEs are particularly important for identifying areas subject to environmental impact – an essential step in establishing future environmental policies that affect human health and environmental protection. Our results offer the most detailed study of surface geochemistry of REEs in Brazilian soils and help expand the limited knowledge available on these elements in Brazilian soil.

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