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Lanthanides in the study of lithologic discontinuity in soils from the Piracicaba river basin

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Abstract

This study was designed with the objective of using lanthanides to confirm the occurrence of lithologic discontinuities, formerly highlighted by morphological and mineralogical studies and recognized by field evidence, in three soil profiles from the Piracicaba river basin, Brazil. Comparison of lanthanide concentrations in the horizons and underlying rocks indicated the presence of allochthonous soils. Application of principal component analysis to the measured elements yielded well-defined segregation into groups with cumulative variances higher than 90% for the first two components. Lanthanides were confirmed as versatile indicators to corroborate parent material discontinuities for the soil profiles studied. © 1998 Published by Elsevier Science S.A.

Keywords: INAA; Lanthanides; Lithologic discontinuity; Parent material; Soil genesis

1. Introduction

A soil within a landscape reflects its own history, since it can be taken as the overwritten record of all the different environmental factors and conditions which prevailed during its formation [1]. The formation of a soil from parent material involves, firstly, the alteration of the primary mineral constituents of the parent rocks by the physical and chemical processes of weathering. Secondly, pedogenesis results in the formation of a soil profile from the weathered rock material, culminating in the development of a mature zonal soil [2]. In addition to weathering, several other factors contribute to the kind of soil that finally develops, including the nature of the parent rock, local topography, climate, the time available for pedogenesis and biological influences, especially human activity [1–3].

Soils are rarely sedentary in the strict sense of being solely derived from the rock material underlying them (autochthonous soil). More often they are formed from material transported by a variety of colluvial, fluvial, glacial, and aeolian processes [1,4], giving rise to an allochthonous soil. In tropical climates, parent material is commonly transported and deposited, leaving a stone line as evidence of this transport [3]. The most common methods used for identifying lithologic discontinuities are examination of clay-free particle-size distributions, sand/silt ratios, index mineral or elemental trends with depth, usually zircon or the elemental equivalent Zr, or Ti/Zr ratios [1].

The composition of the parent material is strictly correlated with chemical, granulometric, morphologic, and mineralogic soil attributes [3]. At first, the trace element composition of a soil will be equal to that of its geological parent material, diverging with time due to the influence of predominating pedogenic processes [2]. On the other hand, the trace element composition of deposited material may diverge markedly from that of the local solid geology and may prove useful in confirming its non-local origin.

Trace element distribution in many environmental compartments has been used in a variety of studies to identify source material [5,6]. Lanthanides, also called rare earth elements (REE), form a subgroup of trace elements with fairly similar geochemical properties, which occur mainly as 3+ cations, show an affinity for oxygen, and are likely to be concentrated in phosphorites and in argillaceous sediments, with the lowest concentrations reported for ultramafic and calcareous rocks [2]. Their geochemistry has been a powerful indicator in mineralogy and petrology, since they possess some characteristics which allow their use as tracers of the pedogenic process [7,8]. REE distribution patterns may yield valuable information about soil profile evolution and the paleoenvironment, and have

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also been used to follow the landscape evolution and weathering history of alkaline rocks in Brazil [9].

An area of the Piracicaba river basin was chosen for this study based on the richness of relief features together with the regionally representative soil types. The original pedogenesis investigation was carried out using the landscape evolution coupled to an integrated geomorphological, geological and pedological study [10,11]. Based on field, mineralogic index, landscape position the authors concluded that some of the soil profiles showed evidence of lithologic discontinuity.

This paper is aimed at combining the evidence from the more traditional morphological, mineralogical and field data with that from the rare earth element concentrations to confirm the presence of lithologic discontinuities in this region.

2. Materials and methods

The study area lies in the Piracicaba river basin, located in the state of São Paulo, southeast Brazil (latitudes 22°42′ and 23°45′W; longitudes 47°30′ and 47°32′S). In geomorphological terms, the area is located in the *Zona do Médio Tietê* of the *Depressão Periférica Paulista* Province, on the banks of the Piracicaba river. Local geology includes the *Grupo Tubarão*, with the predominant formations *Itararé* and *Tatuí*, *Grupo Passa Dois*, with the formation *Irati*, Grupo São Bento, and the Cenozoic sediments. The climate is subtropical C (Köppen classification), with annual average temperatures between 18 and 22°C, and the annual precipitation varying from 1200 to 1500 mm.

Three representative soil types were chosen from the toposequences (Lobo and Morro Grande) described previously [10,11], with well-defined profiles and the presence of a stone line, for the lithologic discontinuity investigation. Profiles A and B were characterized as Typic Hapludox (*Latossolo Vermelho Escuro Álico*), while profile C as Kandiudafic Eutrudox (*Terra Roxa Estruturada Latossólica*). The corresponding underlying rocks to the soil profiles A, B, and C are an argillite of the *Irati* formation, siltstone of the *Tatuí* formation, and a diabase, respectively.

Samples were collected from the horizons of each of the three soil profiles (18, 14, and 10 horizons) until bedrock was reached (depths of 1150, 800, and 700 cm). Only the middle portion of each horizon was sampled in order to avoid mixing at the horizon interface. Following removal of the organic matter and disaggregation, the soil samples were dried at 70°C and sieved to the <63 μm fraction. The underlying rocks were also sampled and samples prepared as described for the soils.

Instrumental neutron activation analysis (INAA) was used to analyze the soil and rock samples to determine the quantities of some rare earth elements (La, Ce, Sm, Eu, Yb, and Lu). Samples of approximately 100 mg (for fractions higher and lower than 63 μm, and certified reference materials IAEA Soil 7 and SD-N-1/2) were subjected to thermal neutron irradiation ($\Phi_{\mathrm{th}}=5\times 10^{12}\ \mathrm{n\,cm^{-2}\,s^{-1}}$) using the IPEN/CNEN/SP research reactor, followed by counting of radionuclides by high resolution gamma-ray spectrometry. Full details of the INAA procedure have already been published [12].

Principal component analysis was applied to the six variables (the concentrations of the lanthanides in each profile) to form a data matrix for each of the size fractions and to find linear combinations to produce new variables known as principal components, using the SAS (Statistical Analysis System) program.

3. Results and conclusions

The first step in identifying the parent material discontinuity was to verify the REE concentrations in the soil horizons and compare them with those of the underlying rocks. Relatively uniform distribution patterns of the REEs within the profiles were observed, as seen by the coefficient of variation of the horizon means (Table 1), with no trends for enrichment or fractionation with depth. However, one distinctive feature between the concentrations of the REEs in the horizons and rocks was noted. In profiles A and B, the concentrations found in the rocks were higher than the average concentrations found in the horizons (Table 1). For instance, such a rock/horizons enrichment ratio in profile A was 2.3–3.4 for La and 1.0–1.2 for Lu, for fractions higher and lower than 63 μm. Conversely, profile C showed lower concentrations in the rock than in the overlying horizons. Thus, such differences in elemental concentrations can be taken as an indication that these soils were not formed from local rocks.

Principal component analysis performed with the concentrations of La, Ce, Sm, Eu, Yb, and Lu measured in the 19 samples of profile A (18 horizons and the rock) resulted in the plot of principal components 1 and 2 shown in Fig. 1. For the <63 μm fraction, the cumulative variance for these two components amounts to 95% of the total variance. The horizon samples are well separated from the rock sample, forming a definite cluster. Similar behavior was found for the >63 μm fraction, with about the same cumulative variance (94%). These visual graphic dispersions were then corroborated by the Euclidean distances which were calculated from the center of the cluster to the rock, and to each horizon. They were found to be 2.8 and 3.8 times higher for the rock than that of the mean distance of the horizons, for fractions lower and higher than 63 μm, respectively. From this, one could consider that the overlying soil may not be formed from the underlying rock, thereby indicating the existence of a lithologic discontinuity.

Likewise, for profile B, the cumulative variance for the first two components accounts for 96 and 95% of the total

Table 1
Lanthanide concentrations ($\mu g\ g^{-1}$) measured in the soil profiles for the two different size fractions. H represents the mean concentration values for the horizons, with coefficient of variation in parentheses. R represents the rock

		Profile					
		A		B		C	
		<63 μm	>63 μm	<63 μm	>63 μm	<63 μm	>63 μm
La	H	20.0 (28)	11.9 (29)	28.5 (31)	17.2 (31)	80.1 (17)	37.4 (22)
	R	46.7	40.4	210	32.0	48.3	42.5
Ce	H	92.7 (13)	45.5 (20)	77.0 (27)	46.4 (19)	163 (9.9)	87.2 (19)
	R	84.6	71.4	227	265	99	79.2
Sm	H	3.16 (24)	1.86 (26)	5.01 (20)	3.00 (26)	18.6 (21)	8.49 (25)
	R	5.7	4.72	33.1	5.78	12.7	10.4
Eu	H	0.58 (26)	0.30 (33)	0.91 (21)	0.51 (26)	4.46 (24)	2.05 (29)
	R	1.01	0.86	5.36	5.27	3.81	3.20
Yb	H	3.86 (11)	2.13 (19)	5.56 (8.8)	3.19 (13)	5.10 (22)	3.22 (44)
	R	4.35	3.05	8.89	8.39	5.05	3.15
Lu	H	0.34 (17)	0.36 (17)	1.03 (12)	0.55 (12)	0.86 (21)	0.52 (33)
	R	0.34	0.45	0.64	0.51	0.78	0.45

variance, respectively, for fractions lower and higher than 63 μm. Much better segregation into groups can be visualized from the plots (Fig. 2) with complete separation of the 14 horizons from the rock. Euclidean distances calculated as for profile A showed values of approximately 4.3 and 4.2 times higher for the rock than in the two soil fractions. Similarly, it is probable that the overlying soil did not form from its underlying rock.

In contrast to the soil profiles A and B, where there is some evidence for discontinuity between the bedrock and the overlying soil type, in profile C the underlying diabase is a compatible parent material for the type of overlying soil (Kandiudafic Eutrudox), thus supposing the existence of an autochthonous soil. Nevertheless, a stone line observed at a depth of 4.7 m remains as a discordant feature to this assumption, since its presence in soil profiles is normally taken as an indication of lithologic discontinuity.

Indeed, the principal component analysis presented peculiar results for this soil. The cumulative variance showed values as high as 93 and 91% of the total variance for the two size-fractions, separation into groups is not as well defined as for soils A and B (Fig. 3). Using the fraction <63 μm, the rock is well separated from the 10 horizon samples (Euclidean distance ratio 3.1). The plot for the coarser fraction (>63 μm) shows that the samples can be distributed into several groups: one for horizons 1, 3, 6 and 7, another for horizons 2, 4, 5, 8 and 9 with

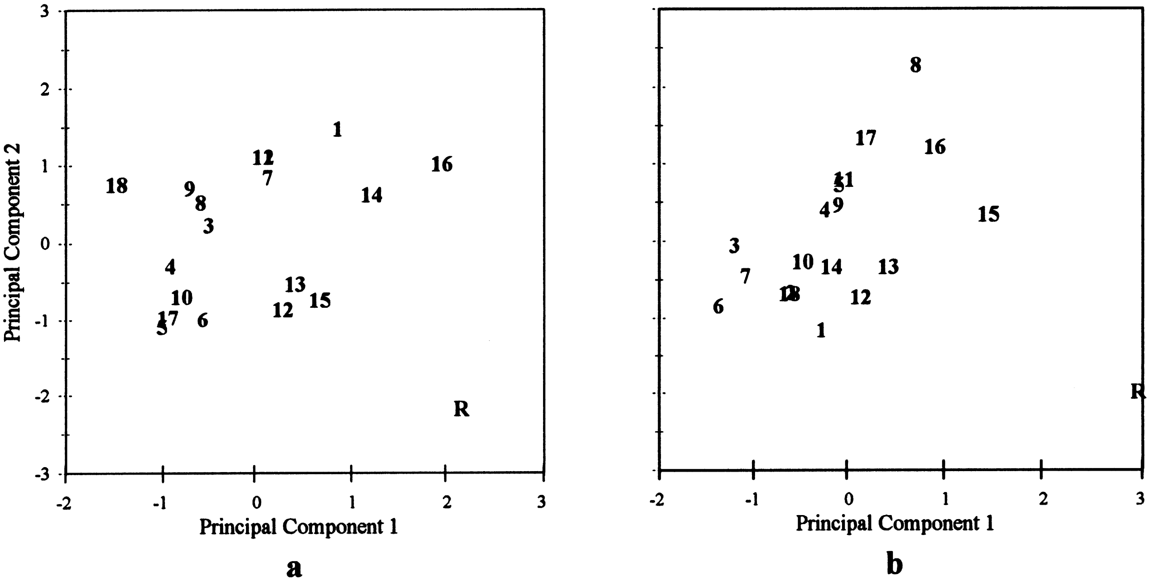

Fig. 1. Plot of profile A samples for the first two principal components using the concentrations of La, Ce, Sm, Eu, Yb and Lu; (a) <63 μm, (b) >63 μm.

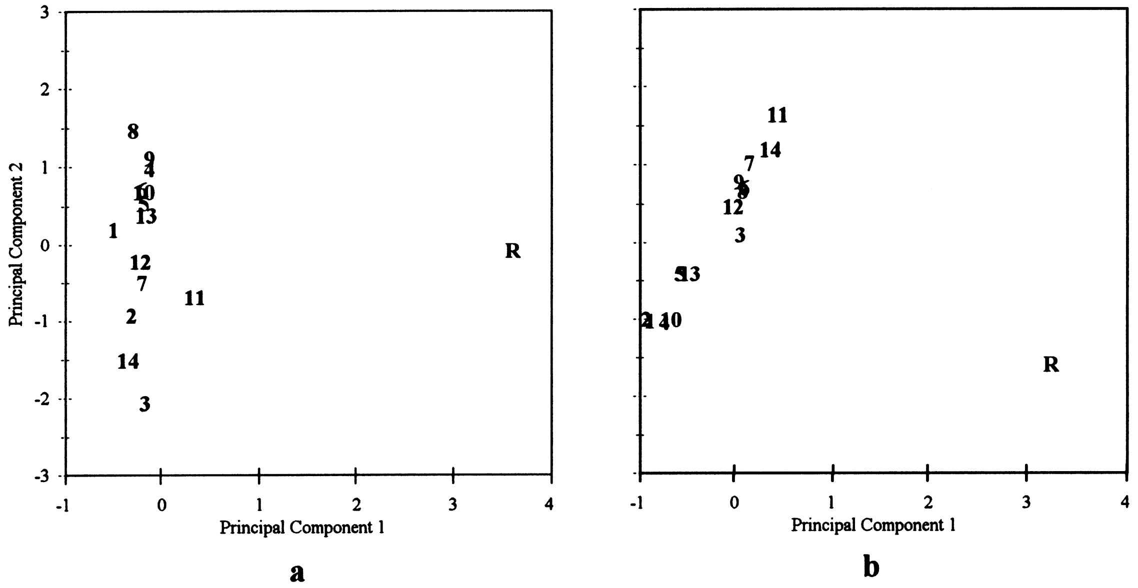

Fig. 2. Plot of profile B samples for the first two principal components using the concentrations of La, Ce, Sm, Eu, Yb and Lu; (a) <63 μm, (b) >63 μm.

horizon 10 forming a third group and the rock a fourth. It may be remarked that this soil profile is formed by a succession of different types of horizons, having Bw (horizons 5 and 7) intercalated with Bt (horizons 3, 4, and 6), a stone line in horizon 8, and C horizon in 9, and a diabase alterite in 10. When studying the evolution of the landscape [11], the behavior of some of the elements (Ti, Zr, and Fe) and their distribution with depth, no discontinuity in parent material could be observed. These authors used detailed morphological description and the statistics of sand size distribution to suggest lithological discontinuity, with our data, based on the rare earth metals La, Ce, Sm, Eu, Yb, Lu, corroborating their conclusion.

There have been many attempts by Vidal-Torrado and Cooper, based mainly on morphological and mineralogical characteristics which were strongly reinforced by field evidence, to achieve a satisfactory confirmation of their hypothesis about lithological discontinuities in the soil profiles studied. Results presented in this paper give support to their conclusions by means of techniques not traditionally used for this type of analysis. We would therefore suggest the future use of rare earth elements as

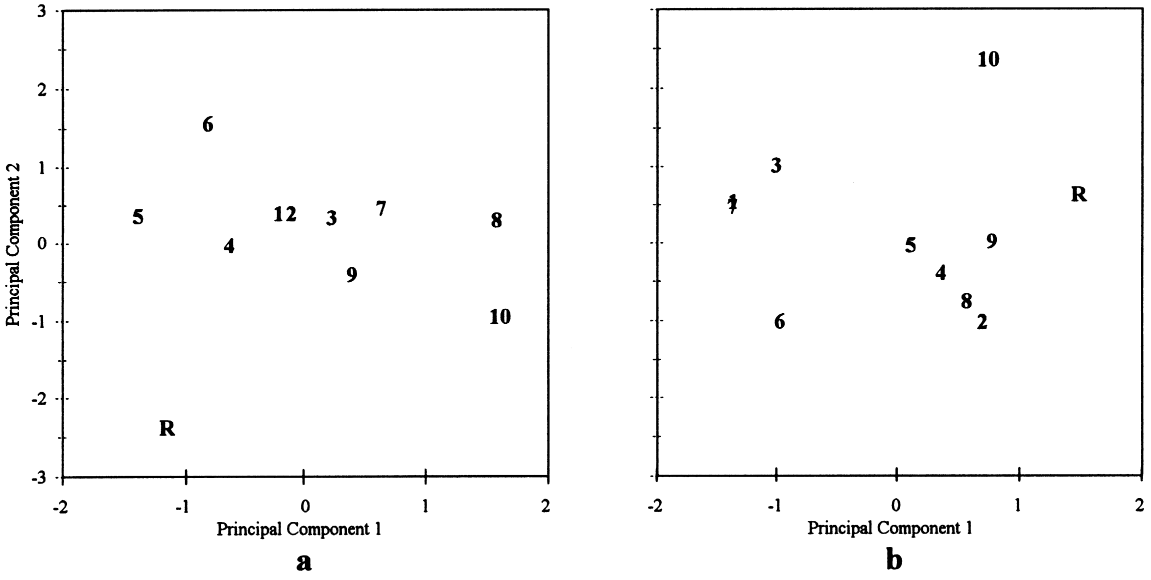

Fig. 3. Plot of profile C samples for the first two principal components using the concentrations of La, Ce, Sm, Eu, Yb and Lu; (a) <63 μm, (b) >63 μm.

another useful indicator for lithological discontinuity studies.

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