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Distribution and fractionation of the rare earth elements in Brazilian soils

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ABSTRACT

The distribution and fractionation of Sc, Y and 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were investigated in 144 samples (topsoil and subsoil) from 88 sites distributed across Brazil. Although, a wide range of natural variability in REE content was observed, overall the REE median contents were relatively low compared with those reported in soils from other parts of the world. The REE contents in Brazilian soils showed significant correlation mainly with Fe, Mn and Ti oxides, as well as organic matter. REE distribution in soils basically depend on the parent material, while fractionation of individual REEs depend on soil characteristics that are partly influenced by pedogenic process. Soils developed from alkaline igneous rocks showed the highest average content of REEs followed by sedimentary rocks, unconsolidated clay sediments, metamorphic rocks, basic igneous rocks, unconsolidated sand and silt sediments, and acid igneous rocks. REE normalized patterns varied significantly within each geological formation, except for soils derived from alkaline igneous rocks. The greatest variations were observed in the light REEs. Graphic inspection using exploratory data analysis tools such as Q–Q normal plots and boxplots was effective to recognize patterns and identify different data groups, determine threshold values and thus define the range of the background REE variability. The data set generated in this study may be used as a preliminary reference for regulatory actions in the Brazilian environmental legislation.

1. Introduction

Natural contents of rare earth elements (REE) in soils are highly influenced by their parent materials, weathering state and pedogenetic processes, texture, and contents of organic matter and clay minerals (Hu et al., 2006). Furthermore, several studies have documented a gradual REEs increase in soils influenced by anthropogenic inputs (Aubert et al., 2004; Hu et al., 2006; Zhang and Shan, 2001). Industrial activities, agriculture and mining have been considered some of the major causes for the increase and redistribution of large quantities of these elements in soil.

In recent years, studies on trace elements including heavy metals, rare earth elements and radionuclides (Andersen et al., 2002; Doelsch et al., 2006; Li et al., 2008; Martin, 1997; Matschullat et al., 2012; Zhu and Shaw, 2000) have gained public attention because many illnesses have been associated with high concentrations of these elements in food and water due to soil pollution. The threat that these elements pose to human and animal health is aggravated by their long-term persistence in the environment. Studies conducted in areas with high REEs concentrations reported that continuous exposure can cause damage to the circulatory, immunologic (Zhang et al., 2000), digestive (Zhang et al., 2000), respiratory (Censi et al., 2011), and nervous systems (He et al., 2008; Zhu et al., 2005), as well as decrease the intelligence quotient in children (Fan et al., 2004), and increase the risk of developing arteriosclerosis and pneumoconiosis (Sabbioni et al., 1982).

World resources of REEs are contained primarily in the minerals bastnäsite, monazite, loparite, and in ion-adsorption clays (U.S. Geological Survey, 2014). Bastnäsite deposits in alkaline rocks and carbonatites of China and the United States constitute the largest percentage of the world's economic resources, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States make up the second largest segment (Foley, 2013). Brazilian deposits account for about 1% of the world reserve (DNPM, 2010).

Currently, the use of REEs is closely associated with high-tech industry. The increasing use of REEs in industrial processes suggests that REE release into the environment is likely to increase in the future with potential impacts on human health (Sadeghi et al., 2013). Under this scenario, it is necessary to establish the natural REEs concentration in soil in order to monitor the impacts of human activity and understand the extent of the anthropogenic influence on the environment.

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Natural concentration of REEs in soils can be used to establish background levels, which allow identification of contaminated areas and contaminants in particular locations. These values are useful guidelines in studies of quantitative risk assessment and in the remediation, recycling and disposal of waste in soils (Gałuszka and Migaszewski, 2011). In Brazil, regional studies on the natural concentration of some trace elements in soils have been used to establish guideline values for environmental quality monitoring (Biondi, 2010; Caires, 2009; CETESB, 2001; Fadigas et al., 2002; Paye et al., 2010). However, there have been very few studies on REEs in Brazilian soils (Pérez et al., 1997), and no REE background level has yet been determined.

The goal of the present study is to determine the natural REEs distribution and fractionation in Brazilian soils at a national scale, investigate the relationship among elements distribution and soil properties, and establish natural backgrounds. Representative soil samples from different Brazilian regions were investigated.

2. Material and methods

2.1. Soil sample selection

Based on the natural occurrence of 11 soil orders and seven type of the rocks a total of 144 samples were selected from a soil bank (Minas Gerais Soil Bank/UFV) to represent the variability in soil types and lithotypes across the different geographic regions of Brazil (Fig. 1), and to ensure that the wide range of physical, chemical and mineralogical characteristics would be covered in the sample set. Selected soil samples were collected from 88 sites (Fig. 2) during field surveys carried out by researchers from the Universidade Federal de Viçosa (UFV) and Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA). It was avoided selecting soil samples sampled from sites near urban environments and industries. The samples included 77 surface horizons (A-horizon) and 67 subsurface horizons (B or C-horizon). These samples were classified according to the Brazilian Soil Classification System (EMBRAPA, 2006) which is based on the World Reference Base for Soil Resources (IUSS, 2006). Surface horizons were defined here as topsoil samples and subsurface horizons as subsoil samples.

2.2. Sample preparation and characterization

All samples were air-dried, gently ground with the aid of a wooden rolling pin, manually homogenized in plastic bags, sieved through a 2.0 mm nylon mesh, and then stored in closed plastic containers. For REE analysis, a representative subsample of approximately 5 g of each soil sample was ground in an agate mortar to less than 0.125 mm mesh,

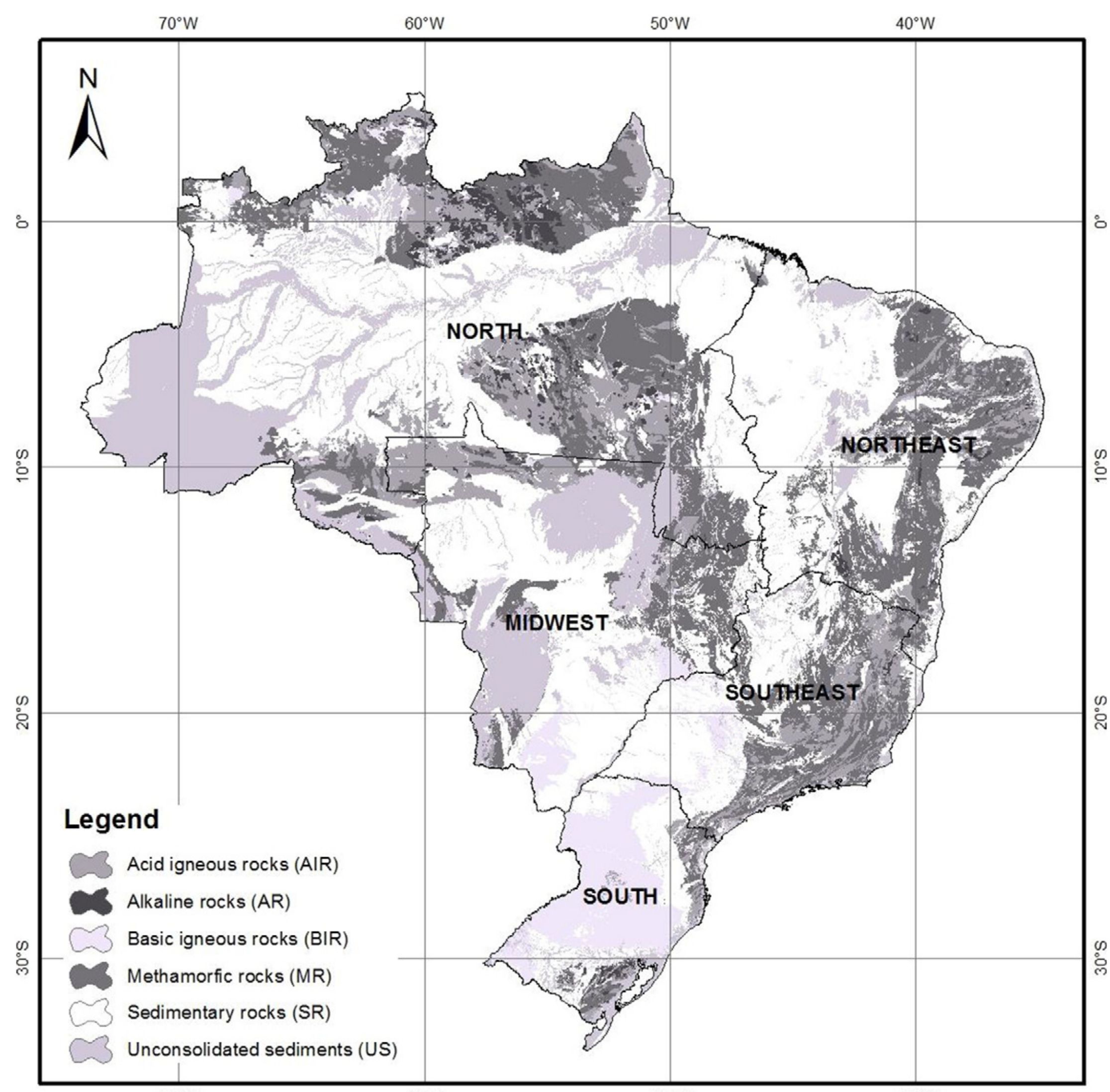

Fig. 1. Simplified lithotypes map at different geographic regions of Brazil.