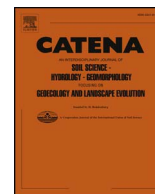




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Rare-earth-element geochemistry in soils developed in different geological settings of Cuba

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ABSTRACT

The increased exploitation of rare-earth elements (REEs) over the past few decades and the disposal of various products containing these elements have prompted numerous environmental studies and the need to establish regulatory guidelines. We determined the concentration of REEs in topsoil samples of 33 soil profiles collected from areas of different geological settings in Cuba. The average REE concentrations revealed the following chemical abundances in decreasing order: Ce > Nd > La > Pr > Sm > Er > Yb > Dy > Tb > Lu > Ho > Gd > Eu > Tm. The significant variation in REE levels reflects the geological diversity of Cuba. The highest REE concentrations were observed in Typic Rhodudalf and Rhodic Eutrodox, which are derived from hard limestone. In contrast, the lowest REE concentrations were detected in the Typic Kandistalf, which originated from mica schist. The lower light REE (LREE) contents in Cuban soils compared with soils from other countries is related to the low abundance of felsic rocks on the island. We also observed a strong positive correlation between REEs and some major elements in soils. This finding implies that the distribution of REEs in soils is partly governed by phosphates and aluminosilicates. The low fractionation between LREEs and heavy REEs is likely related to the predominance of soils developed from carbonates. This finding was also supported by the low La_N/Sm_N and Gd_N/Yb_N ratios and principal component analysis. The spatial distribution of REEs normalized to Upper Continental Crust coupled with univariate and multivariate statistical techniques indicated that parent materials control the prevalence of REEs in Cuban soils. The data presented here represent the first national-wide survey of REEs in Cuban soils.

1. Introduction

Rare-earth elements (REEs) consist of a coherent group of elements (lanthanide series) with similar chemical properties (Henderson, 1984). Based on their atomic numbers and masses, these elements are often divided into two groups: light REEs (LREEs; lanthanum through europium) and heavy REEs (HREEs; gadolinium through lutetium) (Davranche et al., 2016; Hu et al., 2006; Sadeghi et al., 2013; Tyler, 2004). Light REEs are not rare in the Earth's crust ($\Sigma_{\text{LREE}} = 152 \text{ mg kg}^{-1}$); however, HREEs are less common ($\Sigma_{\text{HREE}} = 51.0 \text{ mg kg}^{-1}$) (Tyler and Olsson, 2002). These elements are found in > 200 minerals, mainly phosphates, carbonates, silicates, and iron and manganese oxides (Kanazawa and Kamitani, 2006).

The increasing exploitation and disposal of products containing REEs in recent decades, particularly related to key industrial

technologies (Mihajlovic et al., 2014) and agriculture (Otero et al., 2005), has drawn attention to REEs leaking into the soil. As a result, adverse effects on biota have been observed (Chen et al., 2001; Oral et al., 2010). Establishing REE background concentrations is the first step to differentiating natural from anthropogenic inputs (Fedele et al., 2008) and establishing regulatory guidelines.

Background concentrations and reference values for heavy metals in the soils of Cuba were recently established (Alfaro et al., 2015). Researchers have observed that the geology of this Caribbean country consists of soils that are naturally high in heavy metals compared with other countries (Chen et al., 1991; Salonen and Korkka-Niemi, 2007). On the other hand, data regarding REEs in Cuban soils are scarce and have largely focused on specific conditions and locations (Cabrera et al., 2001; Capote et al., 1997; Capote et al., 1998; Lam et al., 2001; Padilla

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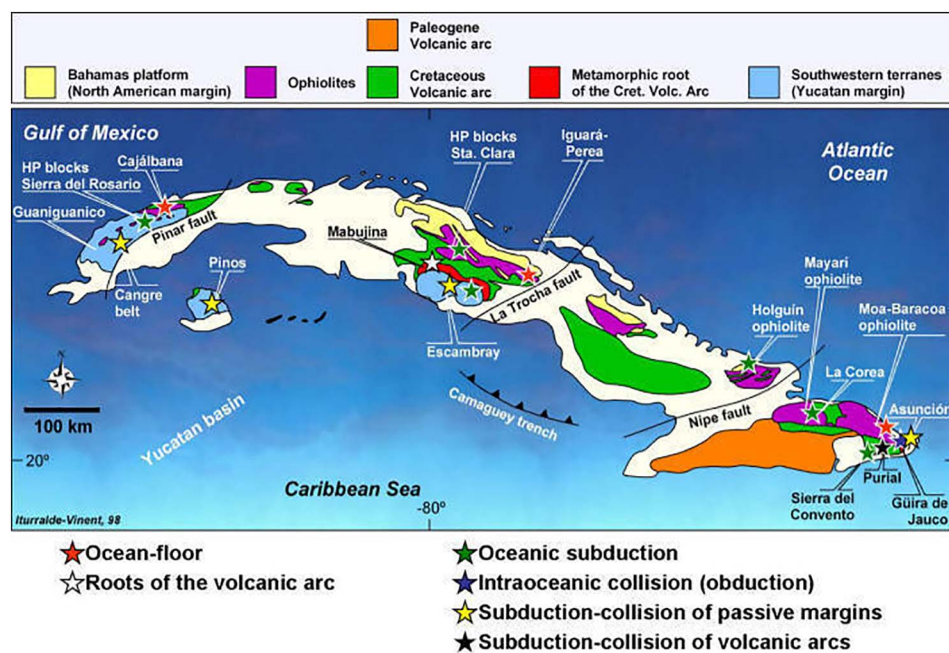


Fig. 1. Cuba generalized geologic map (Iturralde-Vinent, 2011).

et al., 1995; Rizo et al., 2012; Romero et al., 2010) and accordingly do not represent the soil variability on the island.

Unlike other studies to date, we determined the geochemical background and spatial distribution of REEs in Cuban soils collected from different geological settings and free of anthropogenic influence. Consequently, the data present a basis for future monitoring of REE levels in Cuba, a country that is expected to experience substantial economic and industrial changes in the coming decades. Additionally, we have evaluated the geochemical association between REEs and major elements.

2. Material and methods

2.1. Study area

The Republic of Cuba is an archipelago formed by the island of Cuba (104 km²), the Isla de la Juventud (2200 km²), and approximately 4195 islets (Alfaro et al., 2015). Cuba is located in the Caribbean Sea; it is bordered by the United States to the north, Jamaica to the south, Haiti to the east, and the Yucatan Peninsula to the west. Cuba's terrain is mostly plains (75%) with three mountainous regions located in the western, central, and eastern parts of the island. Cuba has a humid, subtropical climate with an average annual temperature of 25 °C in the summer and 20 °C in the winter. The annual rainfall ranges from 316 mm to 1059 mm in the dry and rainy seasons, respectively (Suárez et al., 2012).

2.2. Geological setting

Cuba is the major island in the Greater Antilles and has comprised part of the North American plate since the Late Eocene. According to Iturralde-Vinent et al. (2016), Cuban geology records three remarkable episodes: (1) the Jurassic breakup of North and South America (Pangea) and the associated passive margin and oceanic sedimentary and magmatic evolution; (2) the sedimentary, magmatic, and metamorphic evolution of an intra-oceanic Cretaceous-Paleogene ophiolite-arc complex; and (3) the Paleogene “soft collision” and transfer of the NW Caribbean plate (and Cuba) to the North American plate.

Thick sequences of Jurassic-Cretaceous strata (conglomerates, sandstones, limestones, dolostones, shales) and interlayered basaltic

rocks characterize passive margin sequences preserved in the Guaniguanico terrane and the Bahamas Platform borderlands (Fig. 1). Ophiolitic units present serpentinized harzburgites and dunites, banded and isotropic gabbros, basalts, and hyaloclastites overlain by Late Jurassic through Late Cretaceous oceanic sediments (Fig. 1) (Iturralde-Vinent et al., 2016).

Arc activity in the Cuban segment of the Greater Antilles produced sedimentary, volcanic, and plutonic rocks during the Cretaceous (ca. 135–70 Ma). The sequences of the Cuban arc encompass island-arc tholeiitic, calcalkaline, and alkaline bimodal suites of volcanic and plutonic rocks. Arc magmatic activity is caused by the subduction of Proto-Caribbean passive margin sequences of the Caribeana terrane, an offshore protuberance of the Yucatan (Fig. 1). This activity produced intensely deformed high-pressure metasedimentary and metaigneous rocks ca. 70 Ma once the Caribbean plate started to collide with the North American plate. The collision also created synorogenic basins, an event that continued until ca. 40 Ma. Subsequently, the late Eocene–Recent unconformable post-orogenic continental basins were formed (Iturralde-Vinent et al., 2016).

2.3. Soil sampling

Sampling locations were defined based on the National Map of Cuban Soils, scale 1:25,000 (Instituto de Suelos, 1990), which represents the diversity of the country's soils and their importance to agricultural, urban, industrial and, especially, mining activities. We obtained a total of 33 composite topsoil samples from areas covered by native vegetation or experiencing minimal anthropogenic influence (Table 1); these areas represented a wide diversity of soil orders and parent materials in 13 out of the 15 Cuban provinces. The soils were classified according to the Soil Taxonomy (Soil Survey Staff, 1999). The samples were air dried and sieved on a 2-mm mesh nylon sieve and then ground in an agate mortar and passed through a stainless steel 0.3-mm mesh sieve to homogenize them.

2.4. Analytical methods

For the measurements of the REEs, 1 g of soil was digested in Teflon vessels with 9 mL of HNO₃ and 3 mL of HCl in a microwave oven (USEPA, 1998). All of the extracts were transferred to 25-mL certified

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