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Please cite this article as: L. Torró, J.A. Proenza, T. Aiglsperger, T. Bover-Arnal, C. Villanova-de-Benavent, D. Rodríguez-García, A. Ramírez, J. Rodr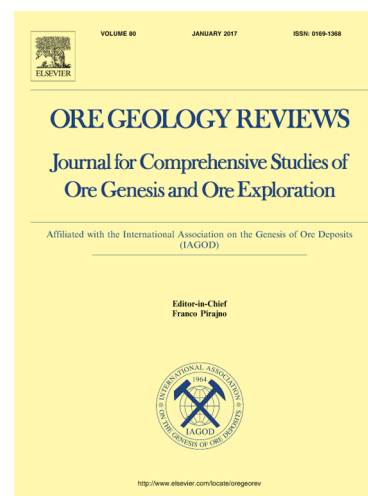íguez, L.A. Mosquea, R. Salas, Geological, geochemical and mineralogical characteristics of REE-bearing Las Mercedes bauxite deposit, Dominican Republic, *Ore Geology Reviews* (2017), doi: http://dx.doi.org/10.1016/j.oregorev.2017.06.017

Geological, geochemical and mineralogical characteristics of REE-bearing Las Mercedes bauxite deposit, Dominican Republic

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Abstract

Bauxite deposits, traditionally the main source of aluminum, have been recently targeted for their remarkable contents in rare earth elements (REE). With ΣREE (lanthanoids + Sc + Y) concentrations systematically higher than ~ 1400 ppm (av. = 1530 ppm), the Las Mercedes karstic bauxites in the Dominican Republic rank as one of the REE-richest deposits of its style.

The bauxitic ore in the Las Mercedes deposit is mostly unlithified and has a homogeneous-massive lithostructure, with only local cross-stratification and graded bedding. The dominant arenito-roundgrained texture is composed of bauxite particles

and subordinate ooids, pisoids and carbonate clasts. Mineralogically, the bauxite ore is composed mostly of gibbsite and lesser amounts of kaolinite, hematite, boehmite, anatase, goethite, chromian spinel and zircon. Identified REE-minerals include cerianite and monazite-Ce, whose composition accounts for the steady enrichment in light- relative to medium- and heavy-REE of the studied bauxites.

Considering the paleo-geomorphology of the study area, we propose that bauxites in the Las Mercedes deposit are the product of the erosion and deposition of lithified bauxites located at higher elevations in the Bahoruco ranges. Based on the available data, we suggest a mixed lithological source for the bauxite deposits at the district scale: bedrock carbonates and an igneous source of likely mafic composition.

Keywords: karstic bauxite; REE; high tech metals; Dominican Republic

1. Introduction

The European Commission (2014) drew up a list of critical raw materials, namely raw materials that have a high economic importance coupled to a high risk associated with their supply. In that list, the REE (Rare Earth Elements) occupy a prominent position as the raw material with the highest supply risk. According to the International Union of Pure and Applied Chemistry (IUPAC), the REE collective name embraces Sc, Y and lanthanoid (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) elements (Connelly et al., 2005). Unique electronic, magnetic, optical and catalytic properties make these elements essential in many manufactured alloys and permanent magnets crucial in industrial and defense electronic systems. As such, REE are in the core of the so-called high-tech technologies, which are appointed to play a major role, for instance, in the green energy alternatives to traditional sources (Hatch, 2012; Van Gosen et al., 2014; Weng et al., 2015; Dutta et al., 2016). Although the control of China over the production of REE has decreased significantly over the past 5 years (98% global production in 2010 vs. ~ 85% in the present; Gambogi, 2017), China's monopoly on this commodity likewise is overwhelming. Supply risk and increasing demand are driving governments and mining companies to promote the exploration for REE in a wide variety of *non-conventional* deposit types including sedimentary and residual ones (Chakhmouradian and Wall, 2012; Eliopoulos et al., 2014; Melgarejo, 2015) as well as

"green mining" alternatives focused on their recycling (e.g. Dutta et al., 2016; Ayora et al., 2016).

Laterite (or residual) ores, including bauxite, formed by extensive weathering of a variety of protoliths, are among the most relevant non-conventional deposits for production and benefit of REE. As Wang et al. (2011) put it, "*bauxite and nickel laterite ores are proposed as the most promising scandium resources for its production [sic.]*". Intense weathering, disintegration of most rock forming minerals and very limited mobility of REE in the weathering environment result in the concentration of these elements relative to their original protoliths, either in secondary REE phases and/or in primary (magmatic) refractory REE-phases and/or adsorbed in residual clays (ion-adsorption clays) (e.g. Mongelli, 1997; Horbe and Costa, 1999; Mordberg, 1999, 2000, 2001; Wang et al., 2000, 2003, 2010; Lanskou and Andreou, 2003; Kynicky et al., 2012; Aiglsperger et al., 2016; Deady et al., 2016). Bauxite deposits, which are currently the main source of aluminum, are classified according to the bedrock lithology as (1) karstic bauxites (overlying carbonate rocks, as in our study case), or as (2) laterite bauxite and (3) Tikhvin types (overlying aluminosilicate rocks) (Bárdossy, 1982). Many karstic bauxite deposits are reported to be relatively enriched in REE (Mongelli, 1997; Mordberg, 1999; Mordberg et al., 2000, 2001; Wang et al., 2003, 2010; Mameli et al., 2007; Eliopoulos et al., 2014; Liu et al., 2016) and often their concentrations are economic as by-products of alumina (Wang et al., 2010; Klyucharev et al., 2013; Deady et al., 2016).

South America and the Caribbean are major bauxite producers and host about the 21% of this resource worldwide (Bray, 2016). In the Greater Antilles of the Caribbean sea, the largest bauxite deposits are located in the central highlands of Jamaica (Nelson et al., 2011). The mineralogy, geochemistry and origin of Jamaican bauxite deposits were mostly published in the 50s to 70s (e.g. Hartman, 1955; Burns, 1961; Waterman, 1962; Hose, 1963; Clarke, 1966; Sinclair, 1967; Comer, 1974). More recently, Wagh and Pinnock (1987) reported significant concentration of REE (e.g., in ppm: 390 Sc_2O_3; 1050 La; 2775 ΣREE) in Jamaican red muds (residue of alumina extraction from bauxite by the Bayer process). Important bauxite reserves exist in Sierra de Bahoruco, SW Dominican Republic. Reserves were initially estimated in 28 MT, with a past production of 4,557,000 tons in the period 1959-1991 by Alcoa Exploration Company

(1959-1983) and Ideal Dominicana (1989-1991) (Nelson et al., 2011). The Las Mercedes deposit, which is located 12 km NE of the town of Pedernales and 185 km WSW of the city of Santo Domingo, is currently the only bauxite deposit under production in the Dominican Republic. The company DOVEMCO resumed production of this deposit in 2013 and reports current reserves of 4,3 MT and an expected operation lifespan of 4 years (Fernández, 2013; DOVEMCO, 2016).

In spite of the growing interest on karstic bauxite deposit as potential, alternative resources of REE and the attested occurrence of important concentration of these elements in Antillean karstic bauxite deposits, the potentiality of Dominican bauxites for the benefit of REE has never been assessed. With that aim in view, we present a detailed petrographic and geochemical characterization of the Las Mercedes deposit, with a particular focus on the REE geochemistry and mineralogy. New data are also used to constraint the origin of bauxite ore in the study area.

2. Geological framework and stratigraphy of the Sierra de Bahoruco

The Sierra de Bahoruco (Bahoruco ranges) in the Bahoruco Peninsula, SW Dominican Republic (Fig. 1A), represents the eastern end of the Presqu'île Du Sud (Southern Peninsula) morphotectonic zone defined by Lewis and Draper (1990). The Sierra de Bahoruco is tectonically limited to the N by the W-E trending Plantain Garden-Enriquillo fault zone; to the E, normal faults associated to the NNE-SSE trending Eastern Beata Ridge Fault sink the mountainous alignment under the Caribbean Sea. Unlikely the northern tectonic blocks in Hispaniola, which began to deform in Eocene time in response to the oblique convergence of the North American plate continental margin and the Caribbean island arc (e.g. Mann, 2007; Escuder-Viruete et al., 2006, 2008), the Bahoruco Peninsula block remained apparently undeformed until the Pliocene times (Pérez-Valera, 2010). The collision of the Greater Antilles belt with the Bahamas Platform arrested the northeastward migration of the Caribbean arc, promoted large-scale topographic uplift and changed the regime to the current left-lateral strike-slip tectonics (Mann, 2007). In the Bahoruco Peninsula, associated transpression resulted in overall contractive structures with a conspicuous strike-slip displacement; high-angle reverse and strike-slip faults and soft, km-scale folds accommodated the deformation (Pérez-Valera, 2010). An integrated study of the

sedimentary tectonofacies allowed to Pérez-Valera (2010) to constrain the progressive uplift and shallowing of the Bahoruco ranges from latest Middle Miocene to the present.

The Sierra de Bahoruco is composed of a thick sequence of Eocene to Quaternary carbonates (Figs. 1B-C) with locally well-developed karst systems (de León, 1989; Pérez-Valera, 2010; Pérez-Valera and Abad, 2010). The sedimentary sequence overlies the basaltic Dumisseau Formation (Fig. 1D), which represents the crystalline basement in the area. In Sierra de Bahoruco, the Campanian to lower Eocene volcanic Dumisseau Formation (formerly Río Arriba Formation: de León, 1989) crops out mainly in topographically depressed areas, in the core of regional scale, NW-SE trending anticlines. In the eastern coastal area, the outcrops relate to normal faults aligned broadly parallel to the coastal line. The Dumisseau Formation consists of a sequence of basaltic flows, pyroclastic deposits and much less abundant sedimentary deposits totaling a thickness of at least 1.5 km (Escuder-Viruete, 2010). This formation, which extends westward to the Chaîne de la Serre in S Haiti, is an on-land portion of the Caribbean Large Igneous Province (CLIP) (Lidiak and Anderson, 2015, and references therein). Escuder-Viruete et al. (2016) determined a mantle plume source for the basalts, which are geochemically classified as low-Ti tholeiites, high-Ti transitional basalts and high-Ti and LREE-enriched alkaline basalts.

The carbonate pile in Sierra de Bahoruco records the progressive shift in the environment of deposition from Eocene deep, outer slope, followed by Pliocene shallow, inner platform and reef boundstones, and to Pleistocene emersion (Pérez-Valera, 2010; Pérez-Valera and Abad, 2010). Carbonate materials in the study zone (i.e. in NW Bahoruco Peninsula), listed below, are representative of the whole sedimentary environment progression. We will use here the stratigraphic correlation and nomenclature after Pérez-Valera (2010). Bottom to top, lower Eocene-Oligocene carbonates include (1) the Aceitillar Formation (Fm. lower-middle Eocene), composed of oncolytic massive limestones, (2) local bioclastic loamy limestones of La Compañía Member (Mb.; middle-upper Eocene) and (3) bioclastic limestones of El Mogote Mb. (upper Miocene-lower Oligocene); and the (4) the Neiba Fm. (Eocene-lower Oligocene), composed of micritic, beige-cream in color, limestones containing silex. A regional stratigraphic unconformity separates these carbonate units of those of the Upper Oligocene-Miocene. The latter consists of (5) loamy, bioclastic and micritic limestones of the Aguas Negras Unit (upper Oligocene); the Pedernales Unit which

includes (6) the Sitio Nuevo Mb. (Oligocene-lower Miocene) warped limestones and calcarenites, (7) the Loma del Guano Mb. (upper Oligocene-lower Miocene) micritic rosy or beige limestones, (8) the Las Mercedes Mb. (upper Oligocene-middle Miocene) rosy limestones with planktonic foraminifera and (9) the Loma de Peblique Mb. (upper Oligocene-middle Miocene) massive rosy limestones; and (10) the Barahona Unit (middle Miocene-Pliocene?) massive limestones with abundant corals and gastropods. Discordantly overlying are (11) the Pliocene-lower Pleistocene La Cueva Unit reefal, bioclastic limestones. Quaternary (Pleistocene and Holocene) carbonates are linked to lagoon and pocket beach dynamics. The position of the carbonate units and members is synthesized in the stratigraphic column in Fig. 1C.

In the study area, Pleistocene-Holocene decalcification red clays and bauxite argillizations (i.e. materials associated to chemical weathering) are spread in (paleo-) erosion surfaces and karst landforms developed on the Eocene-Pleistocene carbonated sequence (Pérez-Valera, 2010). Repeated Pleistocene-Holocene sea-level highstands associated to fast sea-level oscillations (e.g. Thompson et al., 2011; Moseley et al., 2015) favored the development of important alteration profiles and karsitification (Pérez-Valera, 2010). On the other hand, the progressive and continued uplift of the Bahoruco ranges and sea-level lowstands during the same period promoted the erosion of alteration surfaces, transport and deposition in depressed, karstic landforms.

3. Sampling and analytical methods

A total of 23 samples (~1 kg each) were collected at different depths along vertical profiles throughout the mining area.

Major, minor and trace elements of samples were determined at the Actlabs Laboratories (Ontario, Canada) by purchasing the analytical package "4Litho" using fusion inductively coupled plasma emission (FUS-ICP) and inductively coupled plasma emission mass spectrometry (ICP-MS) (for details see http://www.actlabs.com).

Twelve samples were selected as the most representative from two bauxite profiles (A and B), eleven consisting of bauxite and one of carbonate. The samples were carefully ground using agate mortar and pestle, and were manually pressed by means of a glass plate to get a flat surface, in cylindrical standard sample holders of 16 millimeters of diameter and 2.5 millimeters of height. The diffractograms were obtained

in a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg-Brentano $\theta/2\theta$ geometry of 240 millimeters of radius, nickel filtered Cu Kα radiation (λ = 1.5418 Å), and with 45 kV – 40 mA. During analysis, sample was spun at 2 revolutions per second. A variable divergence slit kept an area illuminated constant (10 mm) and a mask was used to limit the length of the beam (12 mm). Axial divergence Soller slits of 0.04 radians were used. Samples were scanned from 4 to 80º 2θ with a step size of 0.017º and measuring time of 50 s per step, using a X'Celerator detector (active length = 2.122º). The sample preparation and analysis were performed in the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB). The software X'Pert HighScore® was used to subtract the background of the patterns, to detect the peaks and to assign mineral phases to each peak, as well as to determine semiquantitatively the mineral phases present in the powder samples.

One bauxite sample (i.e. 100 g of homogenized sample) was selected for the production of heavy mineral concentrates at the hydroseparation (HS) laboratory at the University of Barcelona (http://www.hslab-barcelona.com) by applying the computer-controlled hydroseparation device CNT HS 11 (Rudashevsky and Rudashevsky, 2007; see also http://www.cnt-mc.ru). The proposed methodology for soft rocks by Aiglsperger et al. (2015) was applied. Heavy mineral concentrates from three size fractions (i.e. <30, 30-75, 75-125 µm) were further separated according to their magnetic properties by a FRANTZ magnetic separator. Cylindrical monolayer polished sections (d=2.5 cm) were prepared from each separation product for subsequent investigation.

Mineralogy and textures of bauxites and limestones were studied on 9 polished thin sections, 3 polished sections and 9 monolayer polished sections by means of both transmitted and reflected light petrographic microscopy. Morphological, textural and preliminary compositional features of selected samples were examined by SEM-EDS using an Environmental SEM Quanta 200 FEI, XTE 325/D8395 equipped with an INCA Energy 250 EDS microanalysis system. Operating conditions were an acceleration voltage of 20 kV and a beam current of 1 nA. Chemical analyses of the mineral phases were performed using a JEOL JXA-8230 electron microprobe (EMP) at the CCiT-UB, operated at 20 kV acceleration voltage, 15 nA beam current and with a beam diameter of 5µm. Analytical standards and lines used for analyses were:

wollastonite (Si Kα), apatite (Ca Kα, P Kα), barite (Ba Lα), celestine (Sr Lα), UO$_2$ (U Mβ), ThO$_2$ (Th Mα), GaAs (Ga Lα), YAG (Y Lα), LaB6 (La Lα), CeO2 (Ce Lα), REE-1 (Pr Lβ, Er Lα), REE-2 (Ho Lβ, Tm Lα, Eu Lα), REE-3 (Yb Lα, Sm Lβ, Gd Lα) and REE-4 (Lu Lα, Tb Lα, Nd Lβ).

4. Geology of the Las Mercedes deposit

Bauxites of Las Mercedes, the largest deposit in the Bahoruco ranges, cover an area of 2.31 km^2 and have a rather constant thickness of around 8 to 10 m. The deposit occupies a low-level, peneplain position, and is broadly aligned along the NW-SE trending axis plane of the gentle, regional-scale Las Mercedes syncline (Fig. 1B, D). The deposit presents no sedimentary cover and has a blanket morphology that fills up a huge karst depression developed on bedrock limestones of the Las Mercedes Mb. (Pedernales Unit). The bauxite blanket is only interrupted by random carbonate pillars, corresponding to prominences of the bedrock that protrude from a gentle hummock-shaped to flat base (Fig. 2). High-grade, massive bauxite passes into semi-weathered limestones to the contact with the bedrock limestones and to clayey bauxite or bauxitic clay towards the top (Fig. 3). *Terra rossa* (soft deposit of clay-like appearance, very reddish or brownish-red) covers the karsted surface to a thickness ranging from a few decimeters to two meters.

4.1. Bedrock limestone: textures and facies

Three different facies were recognized in thin sections from samples collected in the Miocene karstified carbonates hosting the bauxite ore of Las Mercedes. The main bedrock facies exhibits wackestone to packstone textures dominated by globigerinids and other planktonic foraminifera (Fig. 4A). The benthic foraminifera of the genus *Nodosaria*, as well as fragments of bivalves, occur. This fossil content indicates a relatively deep, hemipelagic depositional environment. A shallower-water facies characterized by the presence of fragments of colonial corals (Fig. 4B) embedded within a wackestone to packstone matrix, which contains encrusting gypsinid foraminifera, planktonic and benthic foraminifera, coralline algae, peloids and fragments of molluscs and echinoids, was also documented higher up in the succession. The occurrence of fragments of colonial corals indicates a carbonate platform depositional setting. Finally, mudstone textures with scarce tests of the larger foraminifer *Amphistegina*, other

benthic foraminifera and fragments of molluscs and echinoids suggesting more distal platform environments are as well present.

The upper part of the bedrock shows important dissolution features (Fig. 4C) and locally, bauxitic impregnations to a depth of few centimeters. Fractures, dissolution vugs and channels, as well as intra- and interskeletal porosity, are entirely or partly filled with sparry calcite. Skeletal components occurring below the irregular bedrock surface are truncated (Fig. 4B). Locally, the uppermost part of the bedrock corresponds to an authigenic breccia. Accordingly, the Miocene host carbonates underwent ongoing episodes of dissolution and concomitant reprecipitation under subaerial and vadose conditions.

4.2. Bauxitic rock: textures

Bauxites present a homogeneous-massive lithostructure (Fig. 2C, 3B-C), i.e. they are homogeneous in all directions (Bárdossy, 1982), and only subtle, progressive textural changes are observed in the near contact with the bedrock carbonates. Narrow dark red iron-rich crusts of millimeters to few centimeters thick occur at the irregularly-shaped bedrock contact (Fig. 4B); the crusts are made up of an aphanitic matrix with bauxite roundgrains. Above, a pseudobrecciate texture of authigenic origin and an arenito-roundgrained fabric of allothigenic-clastic origin (sensu Bárdossy, 1982) mainly form the bauxitic deposits. Laterally out of the bedrock, the bauxite ore becomes unlithified.

The pseudobrecciate texture results from the brecciation of a dark red pelitomorphic matrix (Fig. 4D). In such fabrics, fissures that vary in thickness from microns to few millimeters, form dense networks in the aphanitic matrix. Fissuring of the pelitomorphic matrix may be related to processes of de-watering (syneresis) or gel compaction (Bárdossy, 1982). Fissures, as well as intergranular pores, are totally or partly filled with sparry calcite. Root traces and fenestrae porosity occluded by blocky calcite also occur. Silt- to sand-sized bauxite particles and roundgrains are common in this texture, as well as mouldic voids of bauxite roundgrains. Scarce ooids occur locally with sizes of less than 0.5 mm in diameter. Ooids have a clastic bauxite particle for nucleus. A complex macropisoid of 2 cm in diameter was also recognized. This single pisoid has a nucleus formed from two micritic carbonate clasts, which occur partly

dissolved (Fig. 5A). Consequently, the pseudobrecciate texture described was also affected by processes of dissolution, reprecipitation and redeposition.

The resedimentation of these bauxite pelitomorphic detritus resulting from the brecciation of the dark red aphanitic matrix documented and of other bauxite deposits gives rise to the arenito-roundgrained texture (Fig. 5B). Accordingly, these bauxite detritus commonly are entirely homogeneous inside. Main textural components correspond to silt- to sand-sized bauxite particles and bauxite roundgrains (up to 1.2 mm in diameter). Subordinate components are ooids (up to 1 mm in diameter) (Fig. 5C), pisoids (up to 1.2 mm in diameter; sensu Bárdossy, 1982), and carbonate clasts, which frequently show dissolution features. Nuclei of ooids correspond to bauxite roundgrains (Fig. 5C) and silt- to sand-sized bauxite particles. Arenito-roundgrained textures locally exhibit cross-stratification (Fig. 5D) and repeated sub-millimetric to centimetric cycles of graded bedding (Fig. 5E). Minor, localized ooidic textures and grainstone fabrics with bedrock-derived calcareous clasts, resedimented fragments of bauxite rocks (Fig. 5F) and coated grains with shell fragments for nucleus occur as well. Small breccias and calcite cements of meteoric and burial origins mainly fill the intergranular space in this texture. Fissures, fenestrae porosity, dissolution vugs and mouldic voids of bauxite roundgrains are normally entirely or partly occluded by sparitic calcite.

5. Mineralogy of the bauxite ore

According to the results obtained by powder X-ray diffraction, gibbsite is the most abundant phase in all the studied samples of both profiles, followed by kaolinite, and minor hematite, boehmite, anatase, chromian spinel and goethite (Figs. 6, 7). The bauxite samples contain variable amounts of gibbsite (29-65 %), and the gibbsite content decreases towards the bedrock (Figs. 6B-D, 7). On the contrary, kaolinite (15-26%), when present, increases towards the bedrock (Figs. 6B-D, 7) so that gibbsite and kaolinite are inversely correlated across the profiles. Hematite, anatase, goethite and chromian spinel are present in all samples across the profiles, always representing less than 15 % of the sample each (Figs. 6, 7). It is worth noting the absence of diaspore and rutile in both profiles. Finally, the bedrock carbonate sample of profile A consists almost entirely of calcite (Fig. 6E). The *terra rossa* samples of profile A contain the lesser amounts of gibbsite (25-29 %) and remarkable amounts of kaolinite (21-23 %), accompanied by quartz (7 %), and the highest boehmite contents (14 %) (Fig. 6A).

Heavy mineral concentrates from bauxite ores contain Fe-Al oxyhydroxide grains (Al-rich goethite?) which occur either as anhedral crystals of sectored plates (Figs. 8A-B) or as rather round-shaped aggregates with variable porosities (Figs. 8C-D). However, these Fe-Al oxyhydroxides are frequently entirely enclosed within Al bearing compounds (Fig. 8E). Small-scaled (<50 µm) subhedral grains of Cr-spinel (Fig. 12F) are rarely observed. In contrast, zircon crystals are fairly abundant within all the investigated size fractions (e.g. Fig. 8G). Zircons grains occur as euhedral to subhedral, stubby to square prismatic crystals, commonly with short pyramidal terminations and aspect ratios of ~1.5 to 5 and lengths of ~75 to 300 μm. Most zircon grains (i.e. near-entire crystals and fragments) present irregular edges and broken crystal faces most probably due to comminution during transport (Fig. 8G).

The identified REE-phases are cerianite and monazite. Cerianite occurs as replacements, or as coating/impregnating fractures and voids within porous aggregates, of subhedral Fe-Al oxyhydroxide grains (Fig. 8H-I).

Monazite-(Ce) is the main REE-phase in heavy concentrates of bauxite ores from the Las Mercedes deposit. It appears as euhedral to subhedral crystals, ~ 30 to ~ 60 µm across, with isometric-highly modified and less abundant tabular shapes (Fig. 9). Monazite grains exhibit irregular, fractured outlines and other abrasion marks such as scratches, cutouts and notches that evidence turbulent transport. Many crystals host rounded, Si-rich (according to EDS analyses) melt inclusions. Monazite is often found in close relationship with zircon crystals forming mixed grains either sharing a common crystal face or as inclusions of monazite within zircon (Fig. 9). The studied monazite crystals have relatively high and homogeneous ThO_2 (av. = 4.19 wt. %; 0.04 a.p.f.u., normalized to 4 oxygen) and low Ca (av. = 0.81 wt. %) contents (Table 1). The concentrations of BaO, SrO and UO_2 are largely below their detection limits. Cerium (av. = 0.44 a.p.f.u.) is the main REE (Fig. 10), along with less abundant La (av. = 0.25 a.p.f.u.), Nd (av. = 0.14 a.p.f.u.), Sm and Gd (both with av. = 0.04 a.p.f.u.). Most monazite EMP analyses showed analytical totals ~ 100 % and near ideal stoichiometry (both A and B site cations total ~ 1 a.p.f.u.).

6. Geochemistry

6.1. Major and trace element geochemistry and geochemical classification

Whole rock major-, trace- and rare-earth element concentration in samples representative of the bauxitic ore, semi-weathered limestone (close to the contact with the bedrock) and bedrock limestone are given in Table 2. The bauxite samples contain broadly constant high Al_2O_3 (38.57 to 49.34 wt. %), Fe_2O_3 (17.89 to 20.28 wt. %) and TiO_2 (2.03 to 2.61 wt. %) concentrations and erratic amounts of SiO_2 (1.11 to 14.87 wt. %). In the SiO_2-Al_2O_3-Fe_2O_3 classification diagram after Bárdossy (1982), bauxites from the Las Mercedes deposit plot broadly along the limit between bauxites *ss* and iron-rich bauxites (Fig. 11). The concentration of alkaline and alkaline earth elements is systematically very low. Low SiO_2, Fe_2O_3, and Al_2O_3, Na_2O and K_2O (<<1 wt. %) in the bedrock limestone indicate that it contains minor or nil argillite components. Major element concentrations in semi-weathered limestones are intermediate between those in bauxites and bedrock carbonates.

A correlation matrix between the analyzed elements is shown in Appendix A. Strong positive correlations between Al_2O_3 with TiO_2 and Fe_2O_3 (Fig. 12) suggest that they behaved as immobile pairs during the bauxitization process. The positive and negative correlations between Al_2O_3 and SiO_2 at low and high Al_2O_3 concentrations, respectively (Fig. 12), indicate concentration of both elements during initial weathering of the limestones and subsequent depletion of SiO_2 as the Al_2O_3 concentrated during the bauxitization process.

Bauxite samples are enriched in all the analyzed trace elements relative to the semi-weathered limestones, and both lithologies present a conspicuous enrichment relative to the bedrock limestones. The bauxite ores have high contents of V, Ba, Sr, Zr, Cr and Ni, at the level of hundreds of parts per million (ppm). Al_2O_3 yields strong positive correlation with most analyzed trace elements (e.g. Be, V, Cr, Co, Ni, Ga, As, Pb, Th, U). In contrast, the correlation is very poor or absent between Al_2O_3 and Zr, Rb and Cs (Fig. 12). However, the values of Rb and Cs strongly correlate with that of SiO_2, suggesting that these elements presented equivalent or proportional mobility during bauxitization. The content of Zr is uneven and does not present clear correlation with any other major or trace element.

6.2. REE geochemistry

The studied bauxite samples from the Las Mercedes deposit are steadily enriched in REE to the semi-weathered limestones and both lithologies to the bedrock limestones (Table 2). Bauxite presents systematic high REE contents (ΣREE, including lanthanoids, Sc and Y, ranges between 1389 and 1629 ppm at an average value of 1533 ppm). LREE (La to Eu: 822 to 1008 ppm; av. = 925 ppm) are conspicuously enriched relative to HREE (Gd to Lu: 144 to 167 ppm; av. = 155 ppm), at nearly constant ΣLREE/ΣHREE ratios (5.5 to 6.6). The concentration of Y is in the range between 361 and 423 ppm (av. = 389 ppm), whereas that of Sc is in the range between 59 to 67 ppm (av. = 64 ppm). Concentrations of individual REE and ΣREE yield strong positive correlations with the Al_2O_3 content, and strong negative correlation with CaO (Fig. 13). The correlation coefficient is systematically equivalent for the ΣLREE and ΣHREE, and hence fractionation of these elements during the bauxitization process is not expected.

Chondrite-normalized REE plot for bauxite, semi-weathered limestone and bedrock limestone samples in Fig. 14 exhibit roughly parallel patterns for the three lithologies. These patterns are characterized by negative slopes as a result of enrichment of the lighter REE relative to medium REE (La/Sm_{CN} between 4.3 and 4.8) and to heavier REE (La/Yb_{CN} between 8.6 and 10.9), and of medium REE to heavy REE (Gd/Yb_{CN} between 1.5 and 1.9). Negative Ce and Eu anomalies are observed in the studied samples from the three lithologies, with Ce/Ce* and Eu/Eu* ratios of 0.6 to 1.0 and of 0.6 to 0.9, respectively.

7. Discussion

7.1. Deposit formation and source material of bauxites

Bárdossy (1982) provided an excellent assessment on the theories about the genesis of karstic bauxite deposits to this time, each connected to a contrasting source or parent material from which bauxites formed. Some of these theories have been superseded, but classic elements for discussion remain intact (e.g. Salas et al., 2004; Mameli et al., 2007; Liu et al., 2013). The most widely accepted genetic model ends include (1) latherogenic theories, i.e. bauxite derives from pre-existing laterites developed on aluminosilicate rocks, which are eroded, transported and deposited over a karsted surface; (2) the *terra rossa* theory, i.e. bauxite forms after *terra rossa*, which is the weathering residue of carbonate rocks older than the bauxite; and (3) the volcanogenic theories, i.e. bauxites result from the *in situ* laterization of volcanic ash fallen on the

limestone bedrock. As stressed by Bárdossy (1982), these ends were proposed in origin to account for a salient characteristic of some individual deposits, but a combination of parent rocks are the most plausible scenario for most bauxites instead.

In the study case, the bauxite deposit occupies a peneplain position and is aligned along the axis of a gentle synclinal (Fig. 1B, D). The karsted surface might be visualized as a local synform sedimentary depocenter, which according to Pérez-Valera (2010) was emerged previous to Pleistocene-Holocene times, i.e. previous to the period of bauxite formation. Weathering products of rocks exposed on the surface in the vicinity of the bauxite region could accumulate on the depressed, karsted surface by intermittent streams after great downpours in a tropical climate. Textures and sedimentary structures in studied bauxite samples strongly point to water-borne transport and (re)deposition, and hence the idea of a passive bauxitization limited to the extreme weathering of the bedrock limestone series is ruled out. The scenario of an intense reworking of the bauxite is in agreement with the conspicuous compositional (chemical and mineralogical) homogeneity of the bulk of the bauxite profiles. Clastic dominant components of allothigenic origin including abundant bauxite roundgrains (pebbles) strongly suggest that the Las Mercedes deposit formed after erosion and re-deposition of lithified bauxites; this observation limits the casuistry to an allochthonous or parautochthonous case relative to the karsted area. Under-ore breccia locally developed on semi-weathered bedrock limestones may represent recent karstification after bauxite deposition, as described in Jamaica by Bárdossy (1982); this conclusion harmonizes with chemical and mineralogical trends observed in the near contact with the bedrock limestone.

Several other karstic bauxite deposits are known nearby Las Mercedes, including the Aceitillar deposit, which was completely mined out in the second half of the past century. In Bahoruco, most of the karstic bauxite deposits other than Las Mercedes are hosted in Eocene limestones (Aceitillar Unit; Pérez-Valera, 2010), and are localized in topographically higher areas to the N, NE and E of Las Mercedes (Fig. 1B-D). Therefore, an erosion and water-borne transport from these higher bauxite deposits downhill to the karsted surface in Las Mercedes is reasonable and plausible; the authors champion that the most likely source or parent material for the bauxite ore in Las Mercedes are lithified, older bauxite deposits hosted in limestones of the Aceitillar Unit.

Nevertheless, determining the primeval parent material of bauxites in the Sierra de Bahoruco region as a whole requires consideration of regional potential sources. On the one hand, regional carbonates, semi-weathered limestones and bauxite ore are characterized by similar chondrite-normalized patterns (including tenuous Ce and Eu anomalies; Fig. 14). This observation suggests that regional carbonates might have had an important control on the global REE composition of studied bauxites. On the other hand, the sustained presence of accessory clastic mineral grains of zircon, monazite and chromian spinel (i.e. hard mineral species resistant to weathering and transport) in the studied bauxites indicates contribution of weathered aluminosilicate rocks of igneous origin. That contribution could be either direct or indirect (i.e. eroded from a laterized igneous deposit, including volcanic ash deposits, vs. eroded from laterized sedimentary deposits of volcanogenic origin *sensu* McPhie et al., 1993). As far as the current absence of laterites (of igneous protolith) in the bauxite region does not rule out its former presence and subsequent complete erosion, this option is considered here. In order to constrain the nature of the bauxite igneous parent rocks, the Cr/Zr and the Ti/Cr and Zr/Ti ratios are widely used (e.g. Özlü, 1983; Ordóñez et al., 1990; Mameli et al., 2007). The relatively high Cr contents of the studied bauxite ore result in high Cr/Zr (av. = 4.1) and low Ti/Cr (av. = 26.4) ratios consistent with a mafic parent rock (Özlü, 1983), and so is the Zr/Ti ratio (av. = 0.01; Winchester and Floyd, 1977).

Determining the primeval source material of Bahoruco bauxites is beyond the scope of this article. Nevertheless, on the basis of the above described geological framework for the Bahoruco peninsula, the authors anticipate only two plausible igneous, primeval sources: the crystalline basement, that is basalts of the Campanian-lower Eocene Dumisseau Formation (Pérez-Valera-2010; Escuder-Viruete et al., 2016), and/or volcanic ash fallen on the emerged Eocene-Pliocene carbonate series. It is actually hard to conceive the magmatic crystallization of monazite in the Dumisseau basalts, and this mineral was not described by Escuder-Viruete et al. (2016); nevertheless, the LREE enrichment of high-Ti transitional and alkaline basalts of the Dumisseau Formation (Fig. 14) would account for the LREE enrichment relative to HREE in the bauxite ore. As for the volcanic ash, quaternary alkaline basaltic volcanism is described across the south-central Hispaniola, apparently associated to the strike-slip tectonic activity along the Enriquillo-Plantain Garden Fault Zone (Fig. 1A) (Kamenov et al., 2011; Lidiak and Anderson, 2015). Accordingly, volcanic activity occurred just north of the Bahoruco

region at the time bracketed for the bauxite formation. Wind-borne volcanic ash fallen on a karst surface was proposed as source material of Jamaican bauxites (Waterman, 1962; Comer, 1974). In order to accurately discern the primeval source material from which bauxites formed in Bahoruco, further work from a larger set of samples including other bauxite ores from the region, and zircon and monazite dating, is needed.

7.2. Rare Earth Element resources

Studied bauxite samples from the Las Mercedes deposit present ΣREE systematically above ~ 1400 ppm and an average value of ~1530 ppm (n=15). These figures place Las Mercedes in the top ranking of REE-enriched karstic bauxite deposits worldwide. The highest ΣREE values given by Wang et al. (2010) for the Quyang bauxite deposit in China are comparable, but the reported REE values are highly erratic from sample to sample (233 to 1992 ppm; av. = 692 ppm). Also erratic are the ΣREE concentrations in other bauxites from China such as the Guandou deposit (84 to 1306 ppm, av. = 627ppm; Liu et al., 2013) and those in western Guangxi (100 to 4491 ppm, av. = 610; Liu et al., 2016), the Schugorsk deposit in Russia (206 to 3009 ppm, av. = 1062 ppm; Mordgerg et al., 2001) and bauxites from Nurra, Italy (56 to 2888 ppm; av. = 496 ppm; Mameli et al., 2007). In bauxite deposits from the Zagros Mountain Belt in Iran, Zarasvandi et al. (2008) report ΣREE values up to 730 ppm. ΣREE concentration in the Las Mercedes ore is higher than average ΣREE concentrations in red mud wastes in Parnassus-Giona (Greece; ΣREE from 728 to 790 ppm, av. = 767 ppm) and Seydişehir (Turkey; ΣREE from 133 to 1777 ppm, av. = 989 ppm), obtained after processing a bauxite feed with ΣREE 646 and 446 ppm (av. values), respectively (Deady et al., 2016, and references therein). In Jamaican red mud ponds, ΣREE concentrations are commonly above 2000 ppm (up to 2775 ppm) after the processing of a bauxite feed with maximum ΣREE of 1075 ppm (Wagh and Pinnock, 1987).

According to Bao and Zhao (2008), concentrations of only 500 ppm in weathering crusts over granitic rocks are suitable for the processing of REE; average ΣREE in the Las Mercedes ore triples this figure. Bauxitic ores, in addition, offer a series of advantages such as huge tonnages and easiness to concentrate that make it appealing over other mineralization styles (e.g. Klyucharev et al., 2013). Likewise, the geometry of the Las Mercedes deposit allows its exploitation by simple open pit mechanical rock excavation by means of a bucket.

As it appears from above, red muds, which are the waste after alumina extraction from bauxite ores by the Bayer process, commonly double or triple the ΣREE concentration of the original ores. Therefore, by-product production of REE from bauxite can be envisaged as a sequenced, two-step flowsheet including (1) the extraction of alumina from a bauxite feed by means of the Bayer process, and (2) extraction of REE from a red mud feed. This approach safeguards the production of alumina.

The extraction of REE from red muds has been increasingly tested and upgraded during the last decade and Borra et al. (2010) describes an extraction of ~ 80 % REE as a result of simple acid leaching. These rates can be further improved by a combined sulfation-roasting-leaching process designed to address the problem of iron dissolution, ideal for iron-rich bauxite ores such as Las Mercedes (Borra et al., 2016). The effectiveness and profitability of the REE extraction process will strongly depend also on the mineralogical expression of REE and other metals in the red muds (Deady et al., 2016, and references therein). Monazite is the main REE-phase found in the Las Mercedes bauxite ore, along with less abundant cerianite. Processing techniques for the extraction of REE from monazite are quite well and long understood (e.g. Crouse and Brown, 1959). Interestingly, recent reviews (e.g. Kumari et al., 2015) coincide to propose a thermal treatment (roasting) previous to acid leaching for the recovery of REE from monazite concentrates, which concurs indeed with the flowsheet proposed by Borra et al. (2016) for the recovery of REE from a red mud, all-in-one feed (i.e., on paper, a previous concentration of monazite would not be necessary).

8. Conclusions

Bauxite ore mined in the Las Mercedes deposit, Dominican Republic, is characterized by relatively high and homogeneous concentrations of REE, with ΣREE systematically above 1400 ppm and averaging 1530 ppm. These figures place that deposit as one of the richest bauxite deposits worldwide with regards to these elements. Identified REE-phases are cerianite and Th-rich monazite-(Ce). Bauxite ore of Las Mercedes might be by-products or coproducts during the production of Al.

Las Mercedes deposit likely formed after erosion and re-deposition of lithified bauxites located at higher elevations in the Bahoruco ranges. On the origin of bauxites

in the Sierra de Bahoruco region as a whole, weathering of regional carbonates could be a significant participant along with a conspicuous contribution of an igneous source of likely mafic composition.

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Table and figure captions

Table 1. Representative EMP analyses of monazite crystals from the Las Mercedes bauxite deposit. Cations normalized to 4 O.

Table 2. Major, trace and rare earth element compositions of analyzed bauxite, semi-weathered limestone and bedrock limestone samples from the Las Mercedes deposit.

Figure 1. (A) Map of the Hispaniola Island showing the location of the studied area and the main fault systems (EPGFZ: Enriquillo-Plantain Garden Fault Zone; SJRFZ: San Juan Restauración; BGFZ: Bonao-La Guácara; HFZ: Hispaniola; SFZ: Septentrional). (B) Geologic map of the studied area (modified from Pérez-Valera, 2010) with the location of the Las Mercedes bauxite deposit (A). (C) Schematic lithostratigraphic

column of carbonates in the studied area showing the location of the Las Mercedes bauxite deposit (A). (D-D') Cross section of the studied area, slightly modified from Pérez-Valera (2010), showing the location of the Las Mercedes bauxite deposit in the edge of the Las Mercedes anticline; the location of the cross section is shown in B.

Figure 2. Field photographs of the Las Mercedes open pit mine. (A) General view of the deposit with the mined out portion (and remaining limestone columns) in the front and the active pit face to the background of the image. (B) The white carbonate columns stand out against the deep-red bauxite; after stripping of topsoil, mining progresses by scrapping off the friable, massive bauxite with an excavator bucket. (C) View of the active pit face; note the massive texture of high-grade bauxite and the rather constant thicknesses of about 10 m.

Figure 3. (A) Representative specimen of semi-weathered limestone picked up close to the contact with the bauxite ore. (B) Detail of the massive texture that characterize the bauxite ore in the Las Mercedes deposit. (C) Isolated Fe oxyhydroxide concretion floating in massive bauxite; the nodule is 3 mm across. (D) *Terra rossa* and soil terrace to the top of the bauxite ore and karsted surface.

Figure 4. Photomicrographs of bedrock and bauxite textures and components. (A) Detail of a bedrock wackestone texture containing abundant globigerinids and other planktonic foraminifera. White arrow points to a test of Nodosaria benthic foraminifera. (B) Close-up view of the contact (yellow discontinuous line) between the bedrock, which exhibits a truncated fragment of a coral colony, and the bauxitic rock. Note the irregular shape exhibited by the contact resulting from dissolution processes, and the iron-rich crust above. (C) Detail of the highly irregular karstic surface (blue discontinuous line) exhibited by the limestone bedrock and the overlying bauxitic deposits. (D) Example of a pseudobrecciate texture resulting from the brecciation of a dark red pelitomorphic matrix. Note the dense irregular network of fissures.

Figure 5. Photomicrographs of bauxite textures and components. (A) Close-up view of a composite macropisoid with a nucleus formed from two partly dissolved micritic carbonate clasts. (B) Example of an arenito-roundgrained texture. Bauxite grains occur cemented by blocky calcite. Note the graded bedding displayed by the bauxite roundgrains. Partly dissolved bauxite particles and mouldic voids of bauxite

roundgrains are indicated with yellow arrows. (C) Close-up view of an ooid present in the bauxite rock examined. (D) Detail of oblique stratification exhibited by the arenito-roundgrained texture. (E) Close-up view of repeated sub-millimetric to centimetric cycles of graded bedding. (F) Clastic bauxite grains cemented by sparry calcite that indicate repeated reworking of bauxite deposits.

Figure 6. Selected X-ray diffractograms of the profile A from the Las Mercedes bauxite deposit, from the carbonate bedrock to the upper, highly weathered, bauxitic levels: (A) sample M-P6-1 (*terra rossa*), (B) M-P1-1 (bauxite far from the bedrock limestone), (C) M-P1-3 (bauxite), (D) M-P1-6 (bauxite close to the bedrock limestone), E) M-P1-5 (bedrock carbonate). Abbreviations: Ant (anatase), Bhm (boehmite), Chr (chromian spinel), Gbs (gibbsite), Gth (goethite), Hem (hematite), Kln (kaolinite), Qz (quartz).

Figure 7. Pie diagrams representing the semiquantitative results obtained by powder X-ray diffraction in profile A (A) and profile B (B). The position of the samples is depicted in the corresponding field photographs.

Figure 8. SEM-BSE photomicrographs of grains in dense concentrates after hydroseparation including Fe-Al oxyhydroxide (A-E, H-I), chromian spinel (F) and zircon (G) grains. In H and I, cerianite occurs as replacement of porous aggregates of Fe-Al oxyhydroxides.

Figure 9. SEM-BSE photomicrographs of monazite grains from the Las Mercedes deposit with isometric (A, D, E) and tabular (B) shapes. Fractured outlines (A) and scratches and notches (B) are common. Many grains host melt inclusions (C, D). (E) Mixed monazite-zircon grain with close intergrowth between the two phases. (F) Monazite inclusion within a zircon grain. Mnz=monazite; Zrn=zircon.

Figure 10. Triangular plots of the REE compositions of analyzed monazite crystals from the Las Mercedes bauxite deposit. Note that Ce is the dominant REE along with less abundant La, and that the concentration of the other REE and Th is remarkably lower.

Figure 11. Whole rock Al_2O_3-SiO_2-Fe_2O_3(t) ternary plot of studied bauxites and semi-weathered limestones; bauxite classification fields are after Bárdossy (1982).
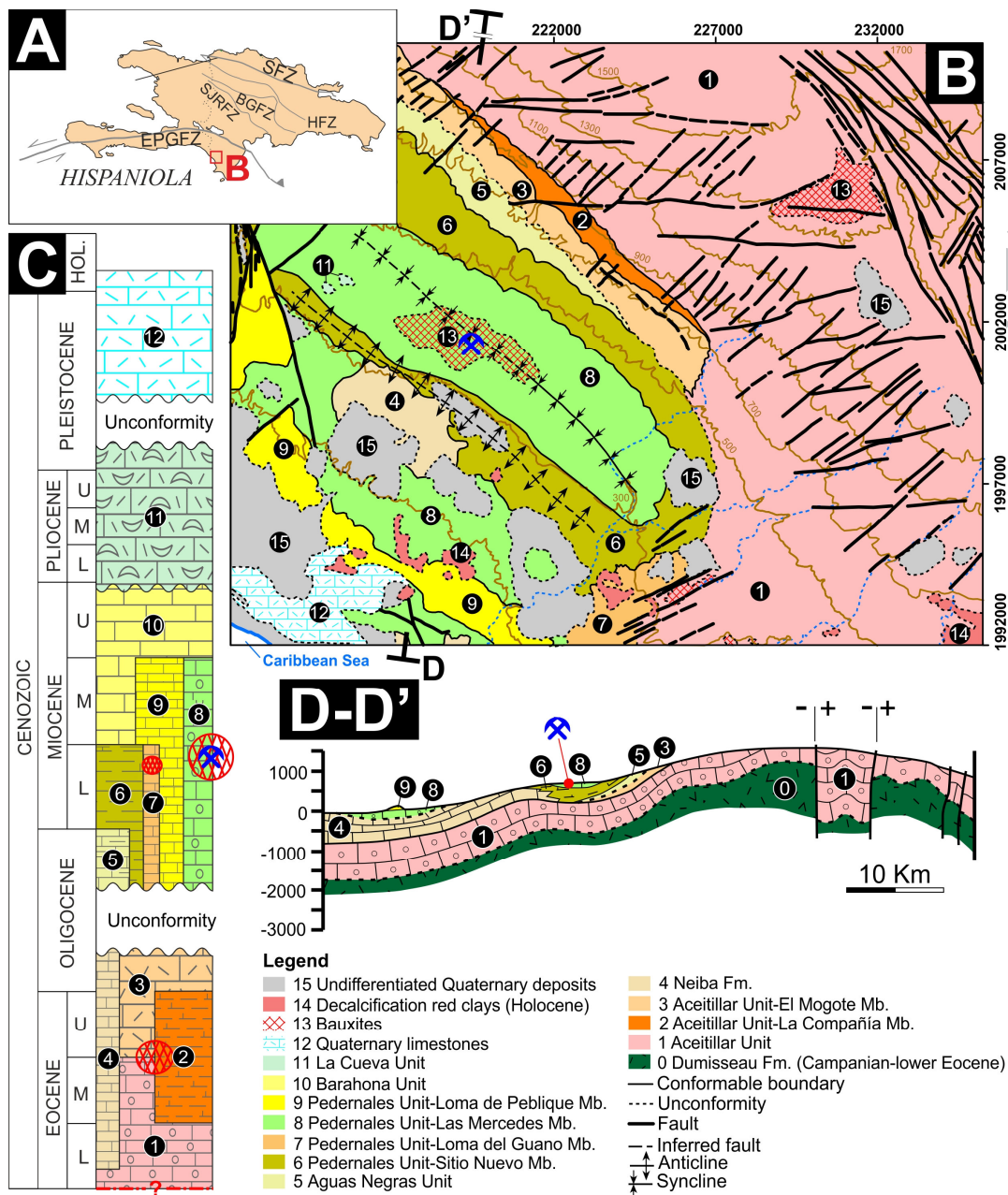
Figure 12. Selected bivariate whole rock major- and trace-element diagrams for bauxites, semi-weathered limestones and bedrock limestones, and inferred trends (red arrows) during the bauxitization process. For further details, see the main text.

Figure 13. Whole rock ΣREE vs. Al_2O_3 and ΣREE vs. CaO bivariate diagrams for bauxites, semi-weathered limestones and bedrock limestones from the Las Mercedes deposit.
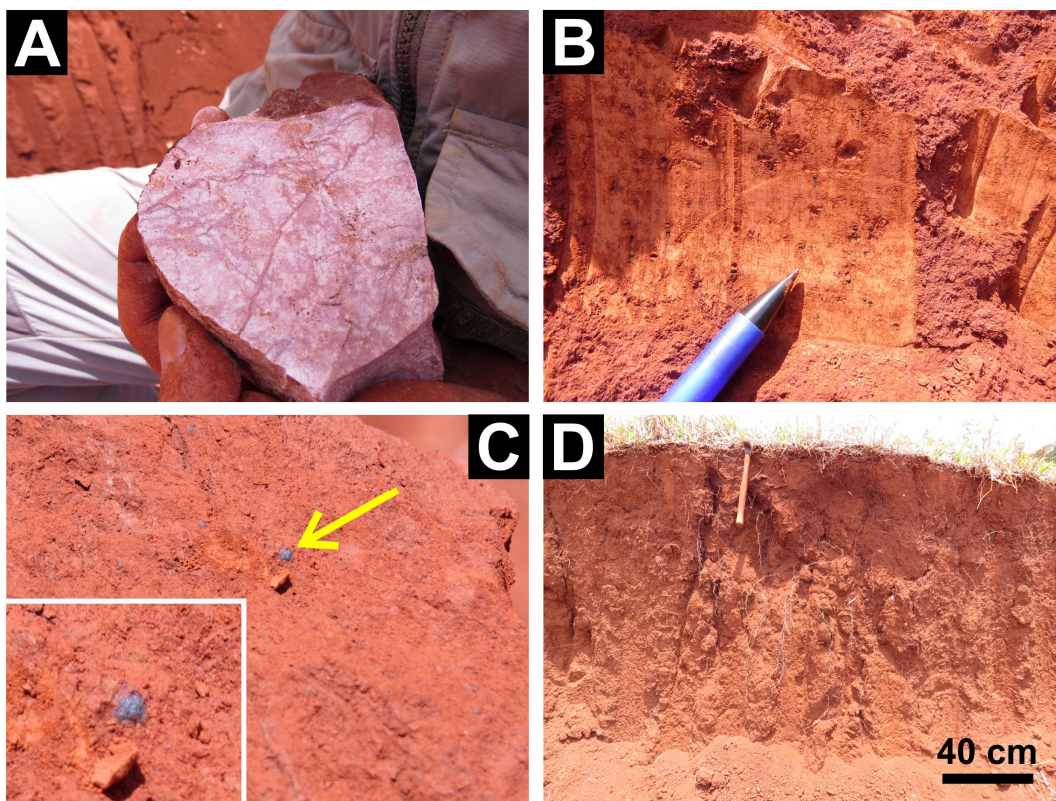
Figure 14. Chondrite-normalized REE plot for whole rock data of studied bauxite, semi-weathered limestone and bedrock limestone samples. Normalization values are after Boynton (1985). The whole rock geochemical data for the Dumisseau Formation lithotypes is from Escuder-Viruete et al. (2016).

Annexes

Appendix A: Table A1. Correlation matrix of chemical element contents of bauxites, semi-weathered limestones and bedrock limestones of the Las Mercedes deposit.
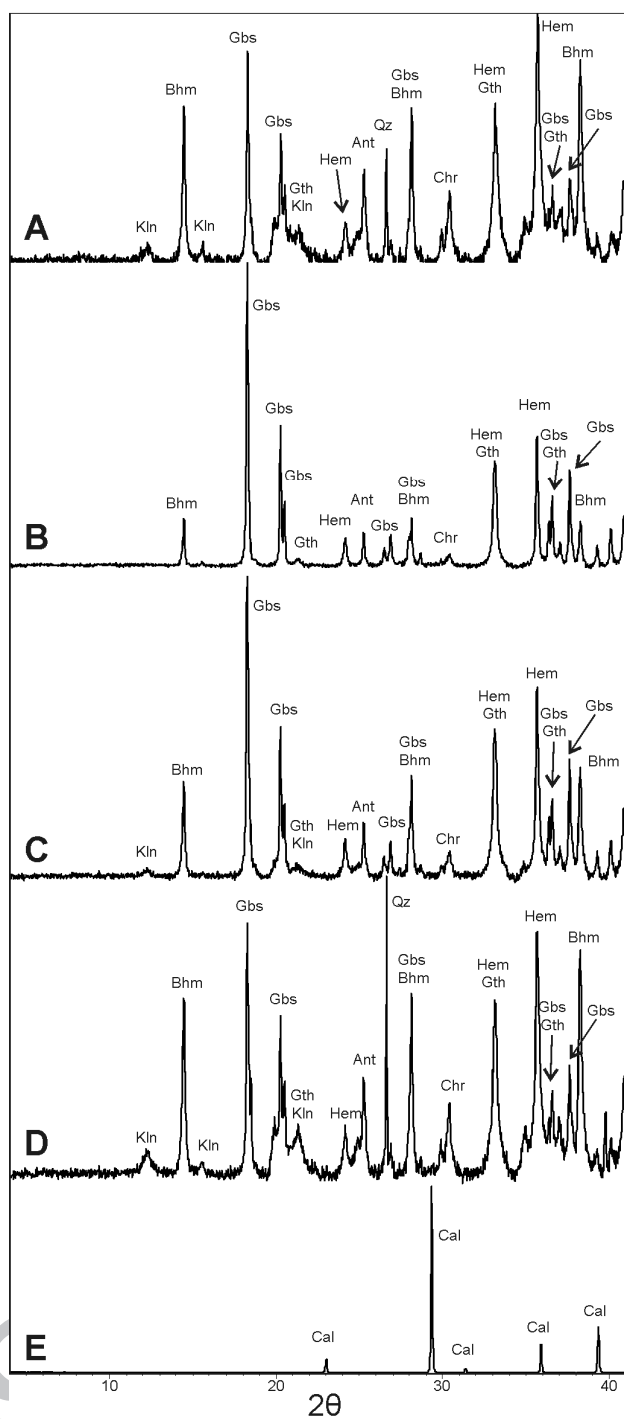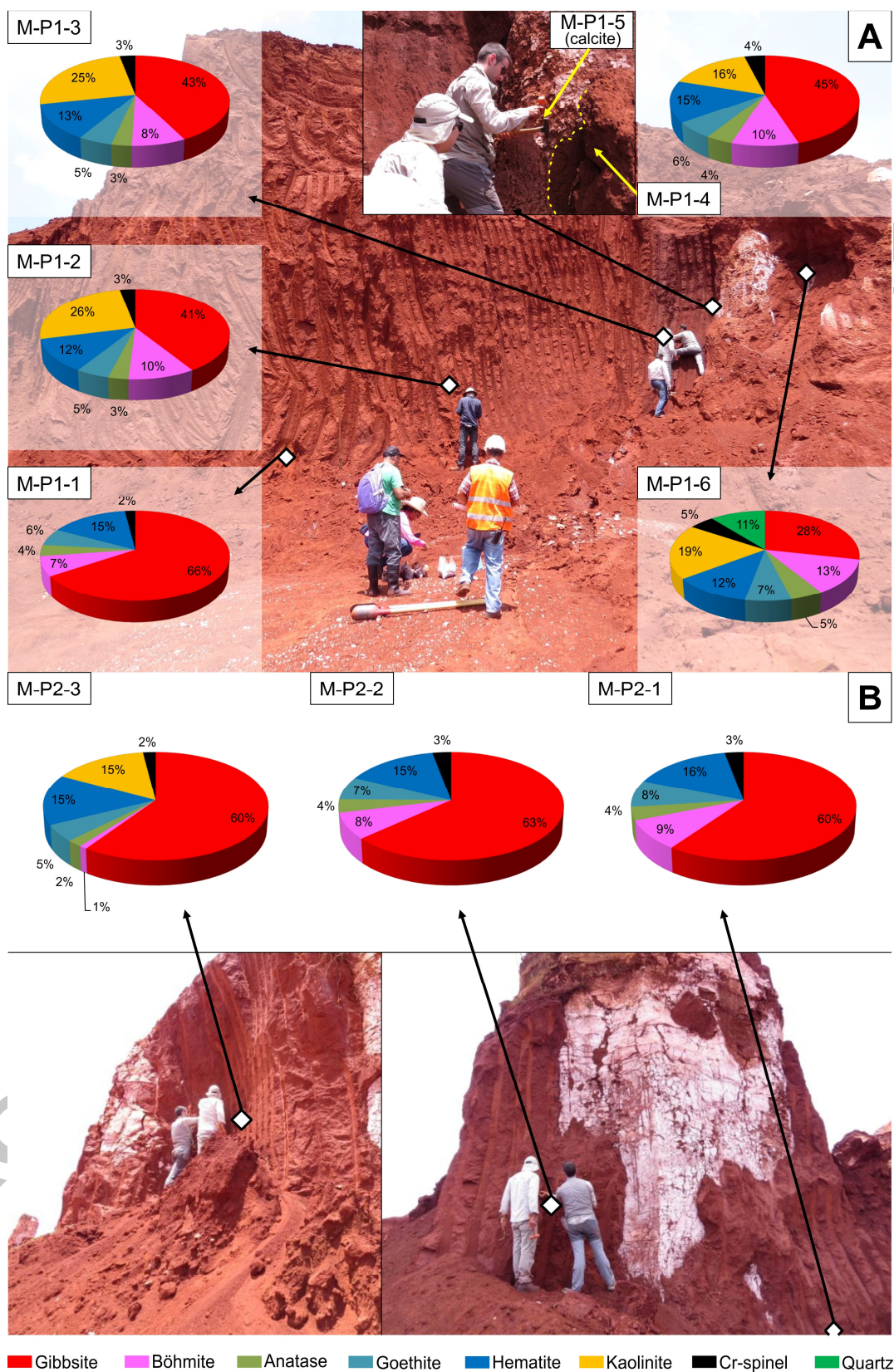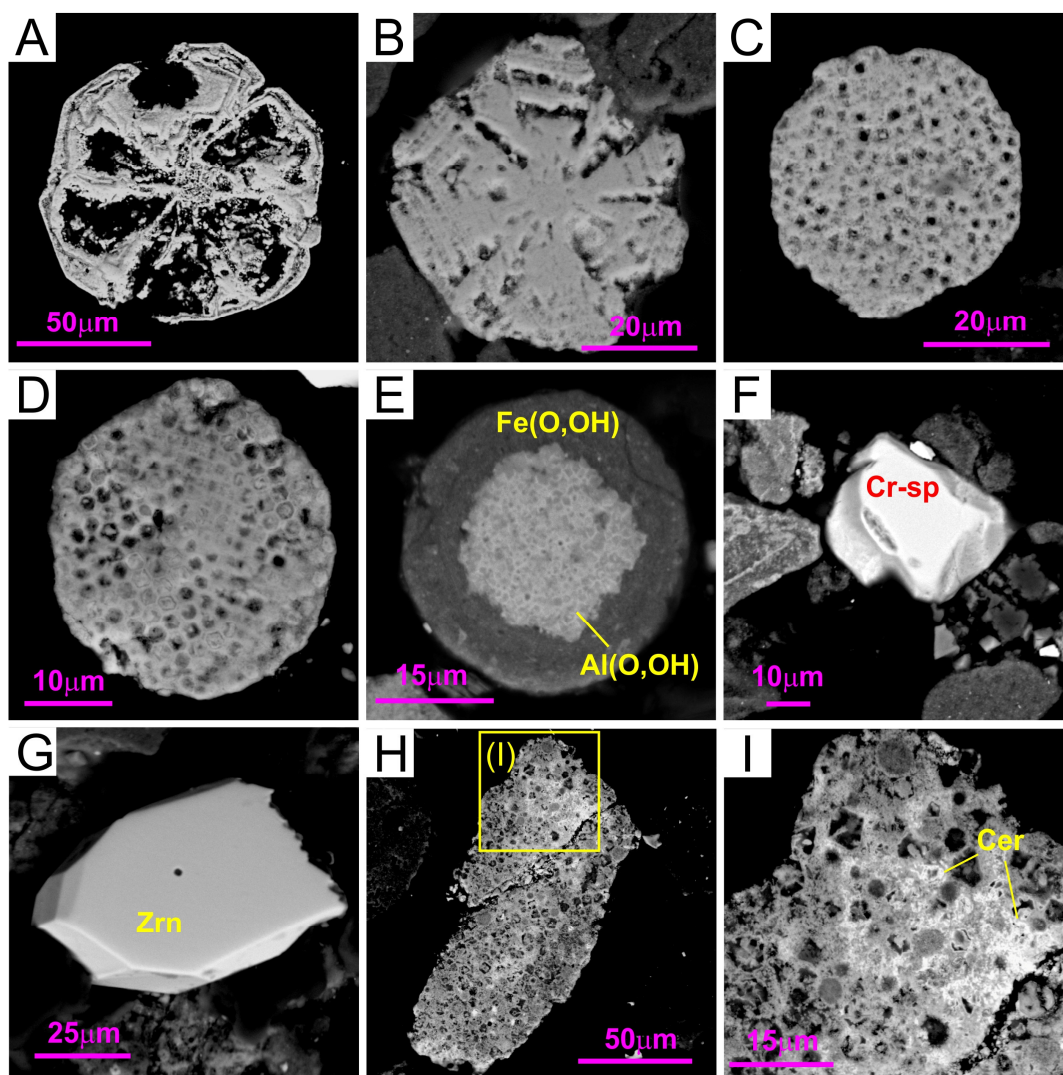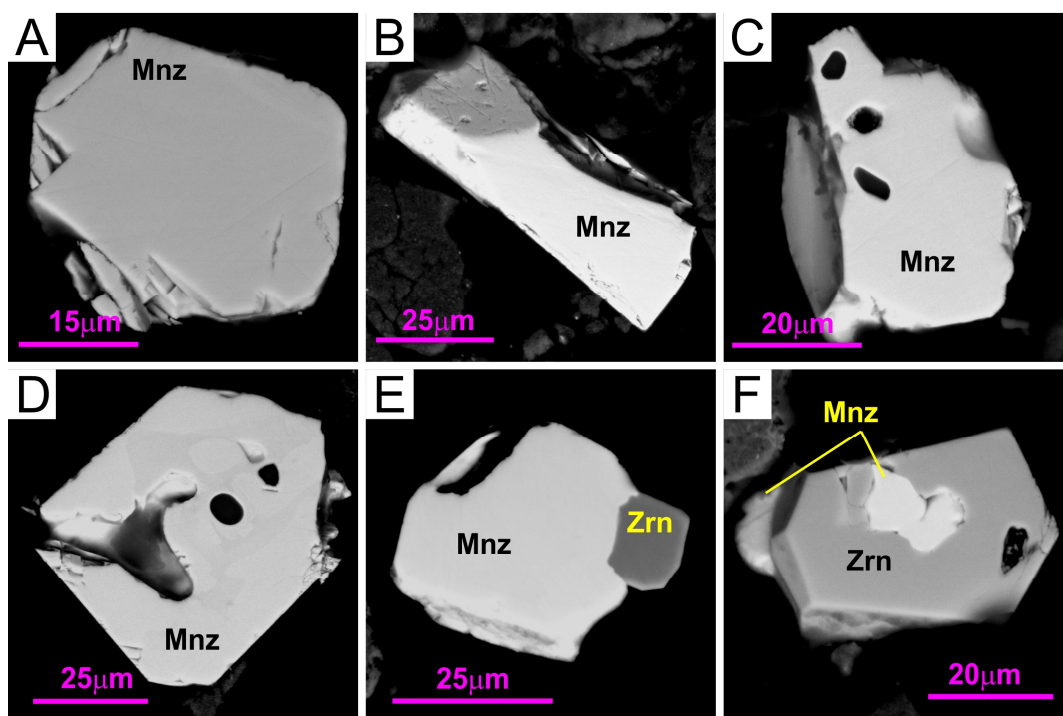
A — HISPANIOLA; SFZ, SJRFZ, BGFZ, HFZ, EPGFZ; B

B — Geological map with coordinates 222000, 227000, 232000 (E) and 2007000, 2002000, 1997000, 1992000 (N); Caribbean Sea; D'–D section line

C — Stratigraphic column; HOL., PLEISTOCENE, PLIOCENE, MIOCENE, OLIGOCENE, EOCENE; CENOZOIC; Unconformity; Unconformity

D-D' — Cross section; elevations 1000, 0, -1000, -2000, -3000; 10 Km

Legend

- 15 Undifferentiated Quaternary deposits
- 14 Decalcification red clays (Holocene)
- 13 Bauxites
- 12 Quaternary limestones
- 11 La Cueva Unit
- 10 Barahona Unit
- 9 Pedernales Unit-Loma de Peblique Mb.
- 8 Pedernales Unit-Las Mercedes Mb.
- 7 Pedernales Unit-Loma del Guano Mb.
- 6 Pedernales Unit-Sitio Nuevo Mb.
- 5 Aguas Negras Unit
- 4 Neiba Fm.
- 3 Aceitillar Unit-El Mogote Mb.
- 2 Aceitillar Unit-La Compañía Mb.
- 1 Aceitillar Unit
- 0 Dumisseau Fm. (Campanian-lower Eocene)
- —— Conformable boundary
- ---- Unconformity
- —— Fault
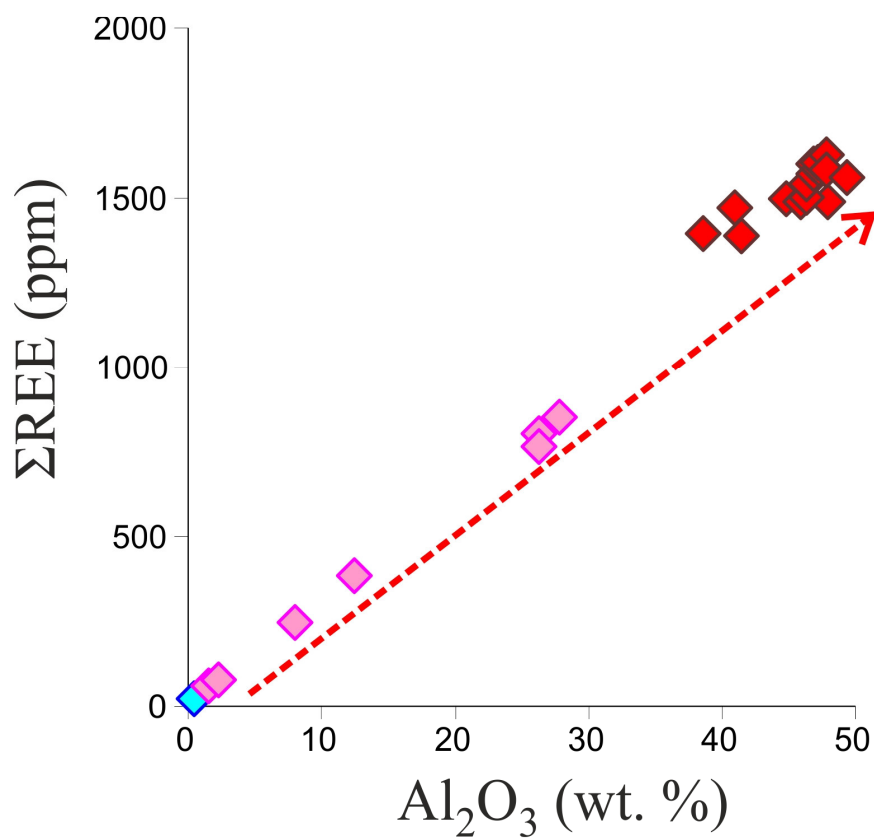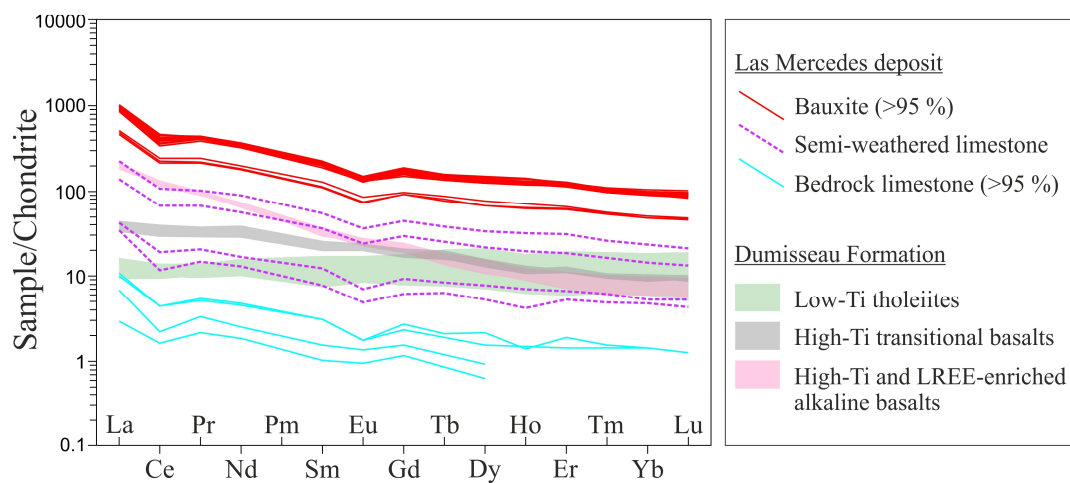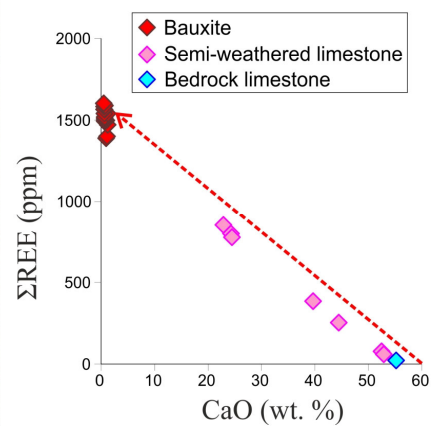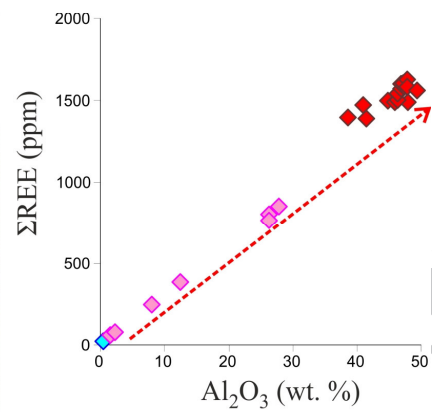- – – Inferred fault
- Anticline
- Syncline

HIGHLIGHTS

- Bauxite deposits may bear important concentrations of REE.
- The las Mercedes bauxite deposit, Dominican Republic, is currently under production.
- Ore has relatively high and homogeneous REE contents (ΣREE > 1400 ppm).
- That concentrations suggest that REE might be benefited as by-product of Al.
- The origin of bauxites in Las Mercedes are most likely lithified bauxites at higher elevations.

Anal.no.	30-75-2_001	30-75-2_009	30-75-2_010	30-75-2_012	30-75-4_008	30-75-4_009	30-75-4_011	30-75-4_013
P_2O_5 (wt. %)	30.14	29.73	30.18	29.77	29.20	29.36	30.04	29.48
SiO_2	d.l.	d.l.	0.44	d.l.	0.66	d.l.	0.44	d.l.
CaO	0.95	0.39	0.95	0.96	0.20	0.13	1.00	1.08
BaO	d.l.	d.l.	d.l.	d.l.	d.l.	0.12	d.l.	d.l.
SrO	0.08	d.l.	d.l.	0.08	d.l.	d.l.	d.l.	0.09
UO_2	d.l.	0.23	d.l.	d.l.	d.l.	0.21	d.l.	d.l.
ThO_2	3.36	4.22	4.25	4.81	4.83	4.91	4.31	4.22
Ga_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Y_2O_3	0.35	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
La_2O_3	17.63	19.45	16.44	16.00	13.79	13.49	16.75	16.39
Ce_2O_3	31.21	30.59	30.68	30.91	29.38	29.37	30.47	31.15
Pr_2O_3	2.86	2.59	2.65	2.67	3.14	3.02	2.68	2.74
Nd_2O_3	10.02	9.35	10.23	10.36	12.97	13.59	10.35	10.43
Sm_2O_3	0.50	0.39	0.60	0.83	1.27	1.39	0.69	0.76
Eu_2O_3	0.50	0.43	0.45	0.53	0.48	0.48	0.47	0.40
Gd_2O_3	2.63	2.72	2.84	2.74	3.14	3.12	2.74	2.78
Tb_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Dy_2O_3	0.17	0.09	0.16	d.l.	0.37	0.45	0.11	0.16
Ho_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	0.10	0.23	d.l.
Er_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Tm_2O_3	d.l.	0.12	0.07	0.21	0.29	0.19	0.12	0.15
Yb_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Lu_2O_3	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	0.06
SUM	100.40	100.30	99.93	99.88	99.73	99.93	100.40	99.89
P (a.p.f.u.)	0.997	0.995	0.996	0.995	0.982	0.994	0.991	0.989
Si	0.000	0.000	0.017	-	0.026	-	0.017	-
Sum B	0.997	0.995	1.013	0.995	1.008	0.994	1.008	0.989
Ca	0.040	0.016	0.040	0.041	0.009	0.006	0.042	0.046
Ba	-	-	0.000	-	-	0.002	-	-
Sr	0.002	-	-	0.002	-	-	-	0.002
U	-	0.002	-	-	-	0.002	-	-
Th	0.030	0.038	0.038	0.043	0.044	0.045	0.038	0.038
Ga	-	-	-	-	-	-	-	-
Y	0.007	-	-	-	-	-	-	-
La	0.254	0.283	0.236	0.233	0.202	0.199	0.241	0.240
Ce	0.446	0.443	0.438	0.447	0.427	0.430	0.435	0.452
Pr	0.041	0.037	0.038	0.038	0.045	0.044	0.038	0.040
Nd	0.140	0.132	0.142	0.146	0.184	0.194	0.144	0.148
Sm	0.007	0.005	0.008	0.011	0.017	0.019	0.009	0.010

Eu	0.007	0.006	0.006	0.007	0.007	0.007	0.006	0.005
Gd	0.034	0.036	0.037	0.036	0.041	0.041	0.035	0.037
Tb	-	-	-	-	-	-	-	-
Dy	0.002	0.001	0.002	-	0.005	0.006	0.001	0.002
Ho	-	-	-	-	-	0.001	0.003	-
Er	-	-	-	-	-	-	-	-
Tm	-	0.001	0.001	0.003	0.004	0.002	0.001	0.002
Yb	-	-	-	-	-	-	-	-
Lu	-	-	-	0.000	-	-	-	0.001
Sum A	1.009	1.001	0.985	1.007	0.984	0.997	0.994	1.021

d.l. = below detection limit

Lithology						Bauxite				
Analyte Symbol	D.L.	M-P1-1	M-P1-2	M-P1-3	M-P1-4	M-P1-6	M-P2-1	M-P2-2	M-P2-3	M-P3-2	M-P3-3
SiO2 (wt. %)	0.01	1.71	5.65	6.59	6.59	12.72	1.43	1.11	4.24	3.76	3.84
Al2O3	0.01	48.69	46.74	46.22	45.86	40.97	47.9	49.34	47.81	46.76	46.31
Fe2O3(T)	0.01	19.72	20.04	19.71	19.69	18.58	19.87	19.53	19.82	19.34	19.6
MnO	0.001	0.594	0.653	0.493	0.514	0.641	0.522	0.593	0.489	0.498	0.555
MgO	0.01	0.07	0.11	0.13	0.13	0.26	0.08	0.07	0.1	0.1	0.1
CaO	0.01	0.29	0.4	0.41	0.41	1.24	0.35	0.39	0.4	0.46	1.09
Na2O	0.01	< 0.01	< 0.01	0.01	0.01	0.04	0.01	< 0.01	< 0.01	< 0.01	< 0.01
K2O	0.01	0.02	0.04	0.06	0.06	0.14	0.02	0.01	0.03	0.03	0.04
TiO2	0.001	2.572	2.455	2.423	2.427	2.082	2.612	2.598	2.55	2.526	2.441
P2O5	0.01	1.21	1.65	1.42	1.39	2.47	1.13	1.22	1.11	1.04	1.53
LOI		24.51	21.14	21.6	21.56	19.03	25.06	24.75	23	23.67	22.82
Total		99.37	98.89	99.06	98.65	98.18	98.98	99.62	99.56	98.18	98.35
Be (ppm)	1	6	6	6	6	6	7	7	6	7	7
V	5	339	337	342	351	295	326	321	349	352	316
Ba	3	139	275	238	230	292	144	126	203	174	185
Sr	2	667	972	816	782	1195	651	726	756	627	869
Zr	4	170	99	116	85	127	536	123	173	253	95
Cr	20	560	580	510	460	550	600	540	660	620	580
Co	1	78	93	68	67	80	70	68	71	67	75
Ni	20	440	570	420	410	500	400	450	430	400	480
Cu	10	160	210	170	160	250	150	180	150	150	180
Zn	30	250	370	330	320	470	240	280	290	310	320
Ga	1	41	43	41	41	39	41	40	41	41	39
Ge	1	< 1	1	1	< 1	1	< 1	< 1	< 1	< 1	< 1
As	5	40	35	30	34	27	31	38	34	36	37
Rb	2	< 2	6	8	8	20	4	< 2	4	4	5
Nb	1	27	23	22	21	21	50	26	26	31	22
Mo	2	3	3	3	3	2	< 2	3	3	3	3
Ag	0.5	0.6	< 0.5	< 0.5	< 0.5	1.2	2.3	0.7	0.7	0.8	< 0.5
In	0.2	0.4	0.3	0.3	0.3	0.3	0.4	0.5	0.4	0.4	0.4
Sn	1	5	4	4	4	4	7	9	5	5	4
Sb	0.5	2.9	3.1	2.9	3	4	2.7	3.4	2.7	2.5	3.4
Cs	0.5	0.5	1.4	2	2	4	0.6	0.5	1.1	1.1	1.3
Hf	0.2	6.7	4.3	4.9	4	5.1	12.2	5.7	6.6	8.1	4.7
Ta	0.1	1	0.5	0.6	0.4	0.7	2.1	0.9	0.9	1.3	0.8
W	1	3	4	3	3	2	5	4	3	3	3
Tl	0.1	0.2	0.2	0.3	0.3	0.7	0.3	0.2	0.2	0.2	0.2
Pb	5	99	93	84	85	78	75	97	94	95	91
Bi	0.4	1.3	1	0.9	1	0.8	1.4	1.3	1.1	1.1	1.1
Th	0.1	31	28.8	28.2	27.2	24.4	30.7	30.7	30.4	29.5	28.7
U	0.1	8.6	7.8	7.1	7	7.1	8.4	8.3	7.7	7.6	8.3
Sc	1	64	65	65	65	65	63	66	66	64	62

Y	2	365	400	391	388	377	392	377	416	423	390
La	0.1	313	302	282	283	279	273	306	312	302	294
Ce	0.1	361	333	311	308	291	317	345	340	333	330
Pr	0.05	53.8	52.5	50.8	50.4	49.8	49.5	52.3	53.8	52.9	51.7
Nd	0.1	217	215	207	204	202	199	210	219	215	212
Sm	0.1	42.3	42	40.2	40.5	40.8	38.9	41.8	44	42.3	42.3
Eu	0.05	10.5	10.6	9.97	10	10.3	9.43	10.2	11	10.8	10.3
Gd	0.1	45.8	46.2	43.6	41.9	43.3	43.5	43.5	48.7	47	45.3
Tb	0.1	7.2	7.3	6.9	6.7	6.8	6.7	6.7	7.5	7.5	7
Dy	0.1	44.7	45.1	43.1	41.5	42.7	41.3	42.4	47.5	46.5	44.3
Ho	0.1	9.2	9.4	9	8.8	9.3	8.7	9	10.3	10	9.5
Er	0.1	24.9	25.9	25.4	24.4	26.5	23.9	24.6	26.4	27	25.9
Tm	0.05	3.2	3.32	3.31	3.14	3.57	3.1	3.21	3.45	3.43	3.34
Yb	0.1	19.3	19.5	19.4	18.6	21.9	19.3	20	20.6	20.8	19.9
Lu	0.04	2.75	2.91	2.78	2.71	3.26	2.69	2.95	2.9	3.07	2.98
ΣREE		1583.7	1579.7	1510.5	1496.7	1472.2	1491.0	1560.7	1629.2	1608.3	1550.5
ΣLREE		997.6	955.1	901.0	895.9	872.9	886.8	965.3	979.8	956.0	940.3
ΣHREE		157.1	159.6	153.5	147.8	157.3	149.2	152.4	167.4	165.3	158.2
ΣLREE/ΣHREE		6.4	6.0	5.9	6.1	5.5	5.9	6.3	5.9	5.8	5.9
(La/Yb)CN		10.9	10.4	9.8	10.3	8.6	9.5	10.3	10.2	9.8	10.0
(La/Sm)CN		4.7	4.5	4.4	4.4	4.3	4.4	4.6	4.5	4.5	4.4
(Gd/Yb)CN		1.9	1.9	1.8	1.8	1.6	1.8	1.8	1.9	1.8	1.8
Ce/Ce*		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Eu/Eu*		0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7

ΣREE = Sc + Y + Σ(La-Lu); ΣLREE = Σ(La-Eu); ΣHREE = Σ(Gd-Lu); (La/Yb)CN = (La/LaC) / (Yb/YbC); (La/Sm)CN = (La/LaC) / (Sm

	SiO2	Al2O3	Fe2O3(T)	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	Be	V	Ba	Sr	Zr	Cr
SiO2	1															
Al2O3	0.44831207	1														
Fe2O3(T)	0.50081036	0.99726192	1													
MnO	0.56699156	0.94842793	0.96026749	1												
MgO	0.83499245	-0.00646826	0.04709369	0.14925235	1											
CaO	-0.53749156	-0.99408764	-0.99851968	-0.96520813	-0.08986592	1										
Na2O	0.44177418	0.04471029	0.07967813	0.07375478	0.56108732	-0.09081384	1									
K2O	0.78493563	0.17323282	0.21914796	0.23502945	0.8546676	0.2475776	0.68882118	1								
TiO2	0.42844135	0.99884036	0.99459772	0.94328423	0.01748611	-0.99060635	0.0455807	0.16327856	1							
P2O5	0.80644331	0.78073415	0.81833243	0.85607799	0.43721911	-0.83543994	0.28616584	0.52691734	0.75759817	1						
Be	0.43721622	0.97106001	0.9755885	0.93897346	0.01326123	-0.96994245	0.13244679	0.22489769	0.96996983	0.80789479	1					
V	0.47479023	0.9950111	0.9943501	0.9503587	0.00965575	-0.99279937	0.0282233	0.16060668	0.99362591	0.77988461	0.95649556	1				
Ba	0.83148437	0.81950705	0.85098976	0.8465013	0.42243582	-0.86702263	0.21205247	0.52623095	0.80143279	0.93933846	0.7909205	0.83279631	1			

Sr	0.75445213	0.85602777	0.88436033	0.89214451	0.33118931	-0.89641419	0.22834826	0.42625663	0.83556622	0.97585331	0.85459393	0.85938095	0.95420563	1		
Zr	-0.01376561	0.53099698	0.51739941	0.49620756	0.11965511	-0.50391871	0.06389291	0.04110179	0.56169901	0.17167179	0.56806005	0.51003119	0.19738672	0.19968264	1	
Cr	0.42064966	0.98173123	0.97849955	0.94540272	0.02310882	-0.97492292	0.04259382	0.12098779	0.98430773	0.73593138	0.95140638	0.98261512	0.77982049	0.82157292	0.58907194	1
Co	0.53730566	0.96445216	0.97453039	0.99177114	0.08847549	-0.97561642	0.05102789	0.19157831	0.95923736	0.84685252	0.94700417	0.96870953	0.85667519	0.90016771	0.48573941	0.96401944
Ni	0.50628865	0.95706399	0.96835423	0.98160059	0.06704077	-0.96528964	0.11990155	0.21074553	0.95271671	0.84220285	0.96682375	0.95421129	0.83241204	0.89120624	0.49788872	0.95473483
Cu	0.71393455	0.90263725	0.92777215	0.95538778	0.31662552	-0.93797567	0.25054695	0.44799067	0.88971041	0.95900041	0.92077223	0.89822804	0.92794069	0.96573703	0.37081737	0.87591221
Zn	0.78662093	0.87319737	0.90207793	0.94612955	0.39251063	-0.91851333	0.20385223	0.43955946	0.86082575	0.94304686	0.86771031	0.88691014	0.94585 28	0.95628254	0.33116387	0.86216094
Ga	0.53000642	0.99322047	0.99562789	0.95927467	0.08156326	-0.99707615	0.07476088	0.23152359	0.99135151	0.81089929	0.95562428	0.99508286	0.86183944	0.88160417	0.51106923	0.97821804
As	0.34907687	0.97897173	0.97091652	0.92903967	0.08297005	-0.96309082	0.05237959	0.10258047	0.98283484	0.70065085	0.95726215	0.97341203	0.72843714	0.78725737	0.55090424	0.97399551
Rb	0.91039298	0.22408 22	0.27593701	0.32778079	0.94032498	-0.31262661	0.61890326	0.94934126	0.21100189	0.61542727	0.24632602	0.23060372	0.62005615	0.52950176	0.00941456	0.18960343
Nb	0.25285438	0.86240947	0.85088941	0.77147065	0.03940235	-0.84172317	0.17215552	0.16601639	0.88020886	0.53445018	0.85978313	0.84082781	0.57817446	0.60553606	0.82784 28	0.87242573
Sb	0.67366875	0.91254154	0.93269954	0.95074825	0.25217783	-0.94246209	0.16549514	0.33204407	0.89724085	0.94510696	0.91379397	0.91266582	0.90421808	0.97496238	0.30912925	0.88359779
Cs	0.98065745	0.37865226	0.43143597	0.49162893	0.89066642	-0.46783108	0.53167543	0.85899073	0.36165 17	0.74781679	0.38716 08	0.39679 25	0.75553345	0.68789621	0.00683143	0.34698991

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Hf	0.18549685	0.80728929	0.79054988	0.69702843	-0.08336397	-0.78090766	0.13798355	0.15231949	0.82669403	0.45363869	0.80441301	0.78265412	0.50347955	0.52251859	0.86825032	0.82565331
Ta	0.08873175	0.72521526	0.70869152	0.62848868	-0.11250349	-0.6972779	0.14735847	0.08274101	0.7473114	0.38622514	0.75326361	0.6922694	0.38730357	0.43565751	0.88347324	0.75168316
Pb	0.42794543	0.98904538	0.98541661	0.95793511	-0.03205776	-0.98247154	-0.00117999	0.10821379	0.98777643	0.76188328	0.95626269	0.99044466	0.79524293	0.84300135	0.49145347	0.98359695
Th	0.42650045	0.99754545	0.99212528	0.94304811	-0.01678686	-0.98876584	0.03307906	0.15355201	0.99894638	0.74939473	0.96197272	0.99312294	0.79604477	0.8312419	0.56245913	0.98689112
U	0.36820804	0.96896286	0.96827025	0.93321043	-0.10626479	-0.96132217	0.00101413	0.07069743	0.96299846	0.79722081	0.97056673	0.95886001	0.77510702	0.85784333	0.47714269	0.94907828
Sc	0.51466388	0.9955684	0.99878695	0.95992723	0.05573328	-0.99839906	0.0900419	0.22494516	0.99174074	0.82869004	0.97311094	0.99314237	0.85977769	0.89339353	0.49711554	0.97581626
Y	0.49627941	0.99163196	0.99504248	0.95467142	0.02548982	-0.99409423	0.0513239	0.17927644	0.98764439	0.82191736	0.9704802	0.99340829	0.85419023	0.89051095	0.48762899	0.97856273
La	0.47230707	0.99506429	0.99525833	0.96512796	0.01163804	-0.99382923	0.04500684	0.16342655	0.99255244	0.80033427	0.96809155	0.99504053	0.82878697	0.87248003	0.49964487	0.9856194
Ce	0.42076916	0.99605676	0.99214861	0.95430425	-0.0299767	-0.98787697	0.04259473	0.14286451	0.9965691	0.758798	0.96853271	0.9923117	0.79259405	0.83669398	0.54718476	0.98889962
Pr	0.49272094	0.99671639	0.9977242	0.96111834	0.02950559	-0.99711747	0.05262612	0.19195061	0.99345995	0.81200411	0.9681422	0.99610375	0.84620825	0.88204521	0.49698749	0.98244103
Nd	0.4927008	0.99640536	0.99804797	0.96193595	0.02938804	-0.99703129	0.0571901	0.1919091	0.99306229	0.8145298	0.9703693	0.99578995	0.84694212	0.88403246	0.4949989	0.9826388
Sm	0.49890853	0.99565495	0.99712923	0.95920436	0.03743982	-0.99661513	0.07172025	0.20106842	0.99257659	0.81285925	0.96741351	0.99525324	0.84787001	0.88419007	0.49150566	0.98344099
Eu	0.51668815	0.99387007	0.99672205	0.95972994	0.05453789	-0.99692932	0.07415669	0.21907437	0.98978	0.82570373	0.96725923	0.99387105	0.86116303	0.89354136	0.48020368	0.98005944

Gd	0.48083 66	0.99551 367	0.99614 244	0.95450 409	0.01905 122	-0.99460 839	0.06410 236	0.18200 05	0.99351 856	0.80072 226	0.96755 203	0.99495 087	0.83947 601	0.87449 474	0.50829 414	0.98735 075
Tb	0.49762 936	0.99503 426	0.99613 689	0.95244 946	0.03296 311	-0.99553 181	0.06157 995	0.19740 571	0.99204 102	0.80815 631	0.96322 095	0.99573 858	0.85224 736	0.88169 406	0.49279 256	0.98367 499
Dy	0.50429 624	0.99341 463	0.99504 582	0.95336 952	0.03560 871	-0.99511 665	0.04646 232	0.19539 615	0.98918 007	0.81782 823	0.96143 878	0.99423 912	0.85847 514	0.88903 924	0.47522 643	0.98041 514
Ho	0.51143 644	0.99135 098	0.99400 699	0.95604 245	0.04405 106	-0.99456 47	0.05290 864	0.19817 896	0.98721 192	0.82177 167	0.96286 738	0.99305 346	0.85900 359	0.89143 926	0.47733 333	0.98180 038
Er	0.53287 194	0.99028 74	0.99550 219	0.96370 806	0.06839 86	-0.99664 003	0.07839 831	0.21801 686	0.98545 658	0.84050 008	0.96796 489	0.99185 033	0.86932 823	0.90474 259	0.47444 067	0.97795 481
Tm	0.55962 312	0.98680 256	0.99409 694	0.96662 224	0.10196 675	-0.99650 055	0.10062 533	0.24807 789	0.98110 864	0.85755 922	0.96777 674	0.98780 673	0.88093 727	0.91691 33	0.46852 393	0.97327 806
Yb	0.55836 506	0.98490 22	0.99215 957	0.97063 371	0.10530 124	-0.99534 022	0.09998 025	0.23959 099	0.97935 919	0.85807 373	0.96729 608	0.98603 818	0.87348 899	0.91588 223	0.47647 307	0.97396 578
Lu	0.57545 144	0.98044 453	0.98923 037	0.97216 007	0.12437 99	-0.99319 28	0.10985 932	0.25762 139	0.97391 762	0.87112 846	0.96680 763	0.98117 509	0.88265 136	0.92555 189	0.45789 708	0.96762 277
ΣREE	0.47883 344	0.99670 842	0.99753 309	0.96080 812	0.01595 025	-0.99595 985	0.05312 349	0.17629 766	0.99409 991	0.80526 736	0.97130 859	0.99621 214	0.83750 07	0.87673 82	0.50519 902	0.98537 133
ΣLREE	0.46222 243	0.99707 395	0.99628 796	0.96130 9	0.00365 791	-0.99405 858	0.04885 901	0.16664 951	0.99534 738	0.79146 77	0.96994 423	0.99556 754	0.82339 254	0.86492 531	0.51514 646	0.98701 465
ΣHREE	0.51277 161	0.99334 073	0.99630 597	0.95972 083	0.04901 028	-0.99662 652	0.06728 271	0.20405 853	0.98945 965	0.82472 891	0.96675 771	0.99397 267	0.85871 309	0.89329 601	0.48584 154	0.98233 764