

# Secondary REE-Minerals in the Karst Bauxites of the Bahoruco Peninsula (Dominican Republic)

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## INTRODUCTION

Rare earth elements (REE) are essential for numerous technological applications. Currently about 90% of the worldwide REE demand is supplied by China (Hatch, 2012), and therefore REE are defined as critical metals (Dutta et al., 2016). Bauxites, the main source for Al in the world, gained interest since they are capable of concentrating significant amounts of REE (Liu et al., 2016), and have been recently considered unconventional deposits for REE (Goodenough et al., 2017). Two types of bauxitic deposits are defined: a) lateritic bauxites (formed after intense weathering of an Al-bearing protolith), and b) karst bauxites (of controversial origin, hosted in carbonaceous rocks). One hypothesis of karst bauxite formation suggests dissolution of the carbonates, whereas the other implies an external contribution of Al-bearing minerals during or after carbonate deposition (Bárdossy, 1982).

Important karst bauxite reserves exist in Sierra de Bahoruco, SW Dominican Republic. The investigated bauxite ores yielded remarkable total REE (La-Lu) contents, from ~400 to ~5000 ppm (average ~1200 ppm), and LREE/HREE ratios between ~1 and ~25 (average ~8) (Aiglsperger et al., submitted; Torró et al., submitted).

The aim of this work is to provide the first detailed characterisation of REE-bearing, secondary minerals from two deposits in the Bahoruco karst bauxite district, Dominican Republic.

## GEOLOGICAL SETTING

The basement of the Bahoruco Peninsula is composed of Campanian to

lower Eocene volcanic rocks of the Dumisseau Fm. (Lidiak and Anderson, 2015), which is overlain by a thick sequence of Eocene to Quaternary carbonate rocks. This sequence records the progressive shift in the depositional environment from Eocene deep, outer slope, followed by Pliocene shallow, inner platform and reef boundstones, and to Pleistocene emersion (e.g. Pérez-Valera, 2010). Uplift of the Bahoruco Peninsula since the Pliocene in response to the oblique convergence of the North American plate and the Caribbean island arc promoted the formation of bauxites on (paleo-) erosion surfaces and karst landforms on carbonates (Pérez-Valera, 2010). The Bahoruco bauxite district is composed of Las Mercedes deposit (active until 2016) and various inactive deposits, two of which have been studied due to their remarkable REE concentrations, Aceitillar and Km 30.

## METHODS

A total of 52 samples collected from the study area were homogenised and analysed at Actlabs Laboratories (Ontario, Canada). Major, minor and trace elements of samples were determined by inductively coupled plasma emission spectroscopy (ICP-OES) and inductively coupled plasma emission mass spectrometry (ICP-MS). The samples were also studied by X-ray powder diffraction (XRD).

Two samples with elevated REE signatures were chosen for a detailed heavy mineral investigation. Each sample (~100 g) was first disintegrated and hand-sieved to achieve three size fractions: <30, 30-75 and 75-125 µm. The two coarser size fractions were

processed by means of hydroseparation (HS) technique and magnetic separation (FRANTZ) at the HS laboratory Barcelona (www.hslab-barcelona.com) (Aiglsperger et al. 2015). Subsequently, polished monolayers were prepared from heavy mineral concentrates and were studied with optical microscopy, scanning electron microscopy (SEM), an electron microprobe (EMP, JEOL JXA-8230, 20 kV, 15 nA, beam diameter of 5 µm). Micro-Raman spectra of the REE-bearing minerals identified in the polished monolayers were obtained (HORIBA Jobin Yvon LabRam HR 800, confocal geometry, 785 nm laser, 100x objective, beam size ~2 µm, 5 measurement repetitions for 10 seconds each). XRD, SEM, EMP and Raman analyses were performed at the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB).

## RESULTS

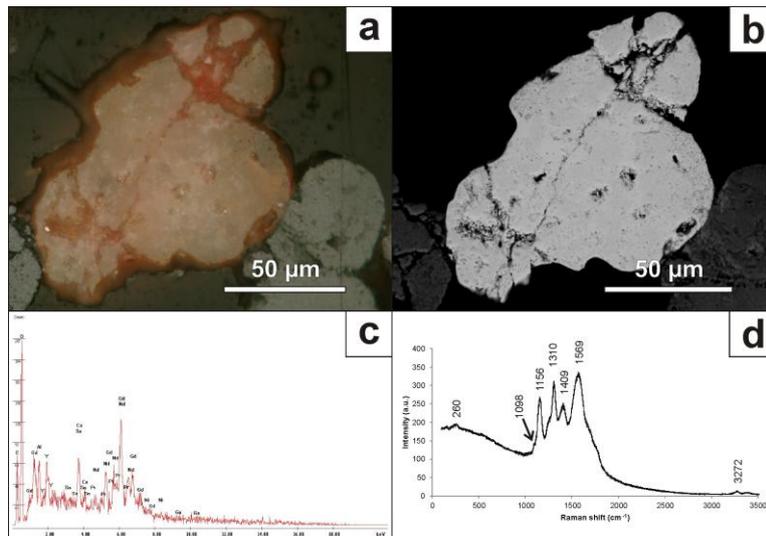
The studied bauxite samples of Bahoruco are mainly composed by gibbsite, with minor hematite, anatase, boehmite and goethite. Primary REE-minerals include monazite-(La,Ce) and xenotime-Y.

The main secondary REE-bearing minerals identified can be grouped into: a) REE-carbonates, and b) REE-phosphates. According to EMP, the most abundant REE-bearing phases are REE-carbonates of the bastnäsite group (Fig. 1), followed by REE-phosphates (rhabdophane, churchite and florencite), and the REE-carbonate tenerite.

REE-carbonates form euhedral crystals, zoned nodules and irregular grains without zoning. Carbonates yield high Gd and/or Nd contents, being

**palabras clave:** Tierras Raras (REE), Carbonatos de REE, Fosfatos de REE, Bauxitas Kársticas, República Dominicana

**key words:** Rare Earth Elements (REE), REE-Carbonates, REE-Phosphates, Karst Bauxites, Dominican Republic



**fig 1** Optical (a) and backscattered electron (b) photomicrographs, energy dispersive (c) and Raman (d) spectra of a bastnäsité-Gd grain from the Aceitillar mining site, Bahoruco karst bauxite district, Dominican Republic.

hydroxylbastnäsité-Gd, hydroxylbastnäsité-Nd, tengerite-Gd and tengerite-Nd the phases identified.

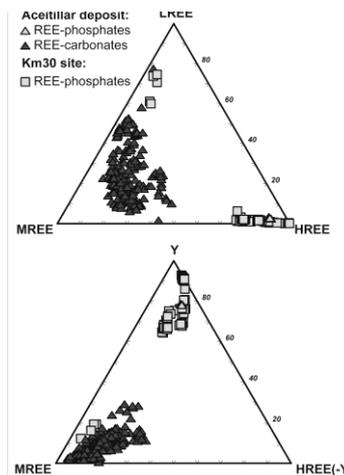
REE-phosphates occur as anhedral single grains or as coatings or vein infills on other grains, mainly Al-oxyhydroxides and asbolanes. Rhabdophane-Y, rhabdophane-Nd, churchite and florencite-Nd were identified.

## DISCUSSION AND CONCLUSIONS

Secondary REE-phosphates and REE-carbonates are clearly secondary, show evidences for REE mobilisation and redeposition as they occur as infills and/or coatings. In general, it is considered that rhabdophane precipitates in the lowermost part of the bauxite profile, under high pH conditions (Berger et al., 2014; Liu et al., 2016). In contrast, according to Eh-pH predominance diagrams, churchite is formed in acidic environments (pH=0.5–3.0) (Liu et al., 2016).

With regards to the distribution of REE within these secondary phases, REE-carbonates concentrate preferentially medium REE (MREE, Sm-Gd), mainly Gd, whereas REE-phosphates are richer in light (LREE, La-Nd) and heavy (HREE, Eu-Lu) REE, especially in Nd and Y (Fig. 2). This, in addition to the abundance of bastnäsité and rhabdophane in the mineral concentrates, is of special interest, because HREE and MREE have a greater economic value compared with LREE.

It is worth noting that hydroseparation, in combination with magnetic separation, is a powerful tool to achieve REE-bearing mineral concentrates.



**fig 2** Ternary diagrams depicting the relative proportions of light (LREE: La, Ce, Pr, Nd), medium (MREE: Sm, Eu, Gd) and heavy (HREE: Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) rare earth elements in the REE-bearing minerals of the studied Bahoruco karst bauxite deposits. Above LREE-MREE-HREE (HREE including Y). Below Y-MREE-HREE (HREE excluding Y).

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