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

/ CRISTINA VILLANOVA-DE-BENAVENT (1, *), JOAQUÍN A. PROENZA (1), LISARD TORRÓ (1), THOMAS AIGLSPERGER (1), ANTONIO GARCÍA-CASCO (2), DAVID RICARDO ALTAMIRANO-MORÁN (1), AUSTRALIA RAMÍREZ (3), JESÚS RODRÍGUEZ (3)

(1) Departament de Mineralogía, Petrología i Geologia Aplicada. Facultat de Ciències de la Terra. Universitat de Barcelona. C/ Martí i Franqués, s/n. 08028, Barcelona, Catalonia (Spain)
(2) Departamento de Mineralogía y Petrología, Universidad de Granada, Campus Fuentenueva s/n 18071 Granada (España); Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR). Avda. de las Palmeras 4, E-18100 Armilla, Granada (Spain)
(3) Servicio Geológico Nacional, Av. Winston Churchill 75, Edificio “J. F. Martínez”. Santo Domingo (Dominican Republic)

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 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 (Bardossy, 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 characterization of REE-bearing secondary minerals from two deposits in the Bahoruco karst bauxite district, Dominican Republic.

GEOLGICAL SETTING

The basement of the Bahoruco Peninsula is composed of Campanian to lower Eocene volcanic rocks of the Dúmsseau 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-) erosive 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 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 xenotone-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 (rhabodophane, churchite and florencite), and the REE-carbonate tengerite. REE-carbonates form euhedral crystals, zoned nodules and irregular grains without zoning. Carbonates yield high Gd and/or Nd contents, being
hydroxybastnäsite-Gd, hydroxybastnäsite-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, on other grains, mainly Al-oxyhydroxides single grains or as coatings or vein infills. REE-phosphates occur as anhedral single grains or as coatings or vein infills. REE-phosphates are richer in light (LREE, La-Nd) and heavy (HREE, Eu–Y) REE, especially in Nd and Y (Fig. 2). 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 bastnasite 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.

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 bastnasite and rhabdophane in the mineral concentrates, is of special interest, because HREE and MREE have a greater economic value compared with LREE.

ACKNOWLEDGEMENTS

This research has been funded by the project 2014-184-133 of the Ministerio de Educación, Ciencia y Tecnología (MESCyT) of the Dominican Government. The authors are grateful to DOVEMCO, the driver Mr. Wilson and assistants Mr. Jhonny and Mr. Lily during fieldwork, and to Dr. X. Llovet for inestimable technical support in EMP sessions.

REFERENCES


