EASILY LEACHABLE RARE EARTH ELEMENT PHASES IN THE PARNASSUS-GIONA BAUXITE DEPOSITS, GREECE

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Abstract

The Parnassus-Giona karst bauxite deposits contain significant concentrations of rare earth elements (400-500 ppm). Preliminary results from a pilot leaching study show that between 19 and 47% of rare earth elements in the bauxite are easily leachable using ion exchange agents such as ammonium sulphate.
Keywords: *Rare earth element leaching, bauxite, Parnassus-Giona.*

Περίληψη

Τα κοιτάσματα καρστικού βωξίτη Παρνασσού-Γκιώνας περιέχουν σημαντικές συγκεντρώσεις σπανίων γαιών (400-500 ppm). Τα πρώτα αποτελέσματα από μια πιλοτική έρευνα ανάκτησης δείχνουν ότι μεταξύ 19 και 47% των σπανίων γαιών στο βωξίτη ανακτώνται εύκολα με χρήση ιοντοανταλλακτών όπως το θειικό αμμώνιο.
Λέξεις κλειδιά: *Ανάκτηση σπανίων γαιών, βωξίτης, Παρνασσός-Γκιώνα.*

1. Introduction

Rare earth elements (REE) have been recently classed as "critical metals" because of rising global demand, due to their use in many new, green and emerging technologies (EC, 2014), and because of a near monopoly (~97%) in supply from China (Chakhmouradian and Wall, 2012; Kynicky *et al.,* 2012). Other countries producing REE, in order of decreasing production are USA, India, Australia, Russia, Thailand, Malaysia and Vietnam (USGS, 2015). In addition there are currently extremely low rates of recycling, less than 1 % (Chakhmouradian and Wall, 2012). These factors increase the urgency to identify alternative REE resources. Most of the world's supply of heavy REE (HREE) comes from around 200 mines working so-called ion-adsorption deposits (or weathered crust elution-deposited rare earth ores) across southern China (Jiangxi, Hunan, Guangdong, Guangxi and Fujian provinces) (Bao and Zhao, 2008; Chi and Tian, 2008). These deposits were formed by *in situ* lateritic weathering of REE rich felsic rocks (mainly granites), which led to the formation of weathered profiles containing residual REE-clays (Kynicky *et al.,* 2012; Moldoveanu and Papangelakis, 2012). A proportion of the REE in these deposits is adsorbed onto the surfaces of clays. REE can be easily removed from the clays using ion exchange agents such as magnesium chloride, EDTA or ammonium sulphate.

Laterites and bauxites are ores formed in tropical soils by weathering processes and are enriched in iron and aluminum, respectively (Retallack, 2010). Some lateritic deposits are also mined for their nickel, gold, niobium, phosphorus and REE concentrations (Freyssinet *et al.,* 2005; Wall, 2014).

Although laterites and bauxites of Central Greece contain REE (Valeton *et al.,* 1987), they are not mined for REE because their concentrations are relatively low. The aim of the current study was to assess the concentrations and leachability of REE in Greek bauxites, which are currently being mined as a commercial source of aluminum, and for which Greece has large reserves (9th country worldwide and 1st in the EU according to the USGS (2015)). Although there have been few studies on the REE potential of Greek bauxites, a number have found significant concentrations in the red mud waste from their processing using the Bayer Process (e.g. Ochsenkühn-Petropulu *et al.,* 1994; Deady *et al.,* 2014; Borra *et al.,* 2015; Gamaletsos *et al.,* 2016).

The main differences between bauxite, red mud waste and ion-absorption clays is that bauxite contains significantly lower concentrations of Si compared with ion-absorption clays, and significantly higher levels of Al compared with red mud. Fulford *et al.* (1991) developed a protocol for the extraction of REE from Jamaican red mud waste using sulphur dioxide. Although this method showed that REE appear to be readily leachable from red mud waste using diluted mineral acids, they cannot be leached from bauxite under the same experimental conditions (Fulford *et al.,* 1991; Binnemans *et al.,* 2013). However, Gamaletsos *et al.* (2016) recently achieved a significant recovery of REE from both Greek bauxites and red muds using acetic acid. The aim of this paper is to present preliminary results from a pilot leaching study of Greek bauxite using an ammonium sulphate [$(NH_4)_2SO_4$] solution as leaching agent.

2. Greek Bauxite Characteristics

The most economically important bauxite deposits in Greece are those of the Parnassus-Giona area (B3 or 3rd bauxite horizon). These belong to the Mediterranean-type allochthonous karst bauxites, which occur as layers or pockets and were formed by lateritic weathering processes (Valeton *et al.,* 1987; Tsirambides and Filippidis, 2012). The mineralogy of these bauxites is dominated by the aluminium oxide monohydrates boehmite [$(\gamma$-AlO(OH)$]$ and diaspore [$(\alpha$-AlO(OH)$]$, the iron oxides hematite (Fe_2O_3) and goethite [FeO(OH)], the titanium oxide anatase (TiO_2), and secondary minerals including kaolinite [$Al_2Si_2O_5(OH)_4$] among others (Valeton *et al.,* 1987; Tsirambides and Filippidis, 2012). The Parnassus-Giona bauxite contains up to 5% of kaolinite as well as lesser amounts of other clay minerals such as illite and chamosite (Tsirambides and Filippidis, 2012; Laskou and Economou-Eliopoulos, 2013). Kaolinite occurs locally as mixtures with Al hydroxides. Low pressure/low temperature alteration of bauxite grains and matrix, possibly aided by down-flowing siliceous waters through pores, cracks and fissures, results in kaolinisation (Dangić, 1988).

Greek bauxite deposits contain an average of approximately 400-500 ppm REE (Ochsenkühn-Petropoulou *et al.,* 1994; Deady *et al.,* 2014). REE are found at both detrital and authigenic REE-bearing minerals in bauxite. The latter are significantly more abundant and usually minute in size (<1 μm), occasionally forming larger aggregates or occurring as micropore and fissure fillings (Maksimović and Pantó, 1996). The authigenic REE-bearing minerals reported at the Parnassus-Giona bauxite are LREE fluorocarbonate minerals of the bastnäsite (($Ce,La)CO_3F$) and parasite ($Ca(Ce,La)_2(CO_3)_3F_2$) group (Gamaletsos et al., 2011; 2016). On the other hand, the detrital ones are the LREE phosphates rhabdophane (($Ce,La)PO_4·(H_2O)$) and florencite ($CeAl_3(PO_4)_2(OH)_6$), and the Y-phosphates churchite ($YPO_4·2(H_2O)$) and xenotime (YPO_4) (Laskou and Andreou, 2003). The crystallisation of authigenic REE-bearing minerals towards the base of the bauxite deposits occurs due to the downward transport of relatively mobile elements (including the REE) (Valeton *et al.,* 1987; Ochsenkühn *et al.,* 1991; Maksimović and Pantó, **1996;** Deady *et al.,* 2014**)**. Although *per descensum* enrichment results occasionally in very high REE concentrations near the limestone bedrock, it is not a standard feature of every bauxite deposit.

3. Materials and Methods

Bauxite samples were collected from the upper parts of Delphi-Distomon S.A. (subsidiary of Aluminium of Greece S.A.) underground mines and were analyzed for their trace element contents by ICP-MS. The B3 (3rd bauxite horizon) active mines were selected due to their importance for the

bauxite exploitation in Greece. Samples Baux 1 and Baux 2 were collected at an altitude of 577 m and 500 m, and at 4.5 m and 9.5 m above the chamber floor respectively. However, both profiles have a greater depth given that "room-and-pillar" mining progresses vertically following the slope of the deposit. Preparation of the samples was carried out at the Camborne School of Mines (Penryn, UK), whilst sample preparation, by lithium borate fusion followed by acid digestion protocol (LF100 analysis for refractory elements and REEs), and ICP-MS analysis was carried out at Acme Labs (Canada).

In order to investigate the potential presence of adsorbed REE cations in bauxite the ammonium sulphate extraction method from the sequential extraction procedure presented in Sanematsu *et al.* (2013) was used. Sanematsu *et al.* (2013) used a modified BCR method of Rauret *et al.* (1999, 2000) for ion-adsorption clays in Thailand. More precisely, they substituted the first step of the BCR method for one using ammonium sulphate, which is also used for cation exchange at many of the mines in China. The first step was carried out at a slightly acidic pH that may also dissolve some of the carbonate. Preparation and analysis of the leachates was carried out at the British Geological Survey (Keyworth, UK). The REE leaching protocol used in the current paper is the following:

1. 1 g of sample is placed in a 50 ml centrifuge tube
2. 40 ml ± 0.1 ml volume of 0.5 M $(NH_4)_2SO_4$ solution added
3. Tube shaken to achieve a suspension
4. Adjust the pH to 4 by adding H_2SO_4
5. 16 h end-over-end shaking
6. Centrifugation of tubes for 20 mins at 3000 rpm (or until supernatant/solid separation is obtained)
7. Allow any residual suspended solid to settle for 15 mins
8. An aliquot from the tube is sampled and the sampled eluate is filtered through a 0.45 μm filter
9. The filtered solution is acidified using HNO_3 and analysed for REE with ICP-MS

4. Results

The two Greek bauxite samples are enriched in light REE (LREE) with approximately 600 ppm of REE in total. The extraction by 0.5 M $(NH_4)_2SO_4$ at pH4 leached 19% (114 ppm) and 47% (278 ppm) of total REE from Baux 1 and Baux 2 samples, respectively (Table 1). Chondrite normalized REE patterns of both bauxite samples and their leachates show a positive Ce anomaly and a negative Eu anomaly, which seem to be common in the Parnassus-Giona bauxites and red muds (Ochsenkühn-Petropulu *et al.*, 1994; Laskou and Andreou, 2003; Deady *et al.*, 2014). Chondrite-normalized data plotted on a graph also show that a higher proportion of LREE can be leached compared with HREE (Figure 1). Leaching results show that the two samples have significant differences in the proportion of the REE being leached. More precisely, ammonium sulphate leached almost the same proportion of HREE (19%) from the two bauxite samples, whereas it leached higher amounts of LREE from Baux 2 sample (52%) compared with those of Baux 1 sample (19%). Nevertheless, the total REE amount leached does not reach the 500 ppm of leachable REE that is required by Bao and Zhao (2008) to satisfy the definition of ion-adsorption ore.
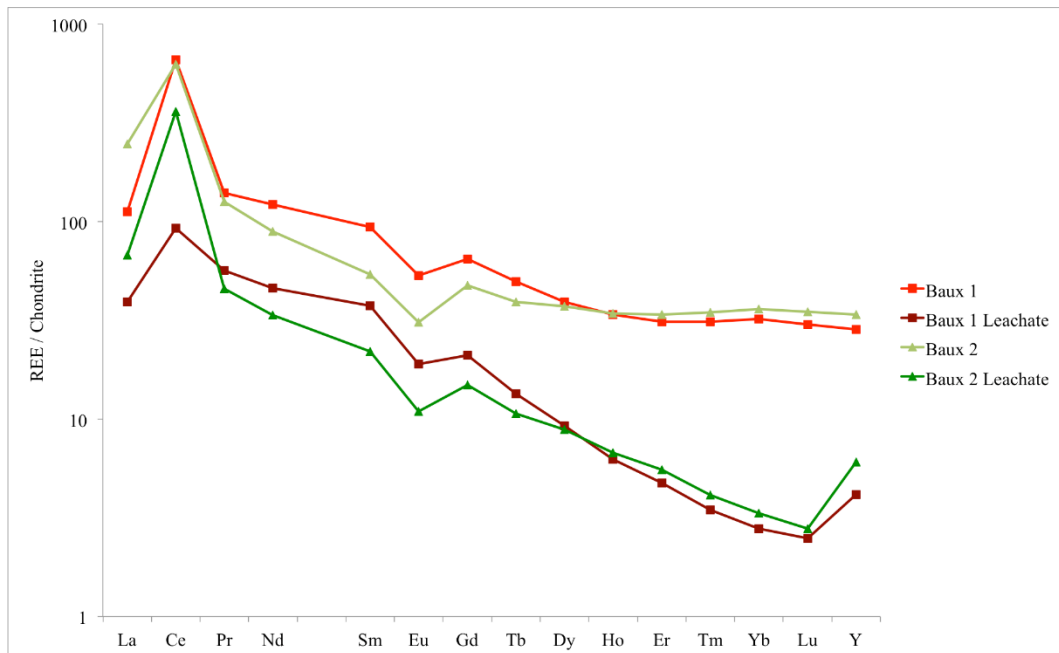
Figure 1 - Chondrite-normalized (McDonough and Sun, 1995) REE patterns in Greek bauxite samples and leachates.

LREE occur as very fine, crystalline, slightly soluble LREE carbonate/hydroxycarbonate minerals in the bauxite samples leached, usually forming clusters or filling micropores and fissures (Figure 2). Ammonium sulphate is supposed only to exchange cations from the surface of minerals and not dissolve them. However, at the leaching experimental conditions of this study (pH 4), it may have caused some dissolution of these minerals. Consequently, preferential LREE fractionation into solution, relative to HREE, may have been caused by a partial dissolution of the LREE minerals in the bauxite. In addition the lanthanide contraction that controls the grouping of LREE and HREE into different mineral hosts may also have an effect on the cation exchange behaviour.
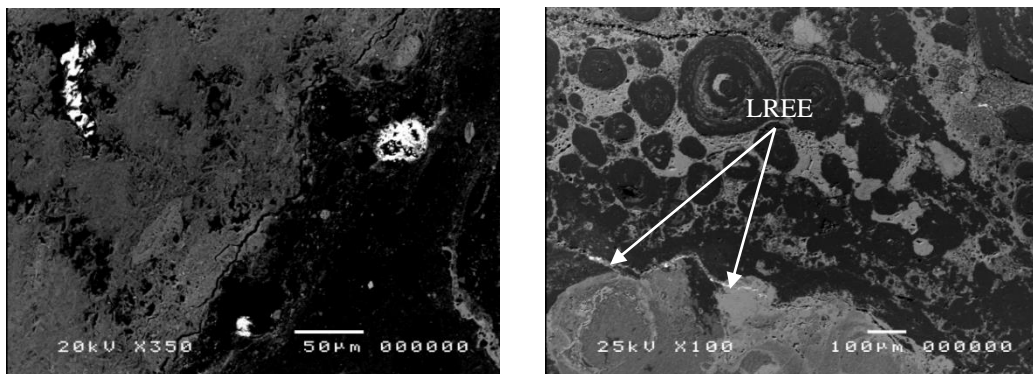

Figure 2 - BSE-SEM images of LREE carbonate/hydroxycarbonate minerals in Greek bauxite samples (Wall *et al.,* 2014).

5. Discussion

Concentrations of REE in Greek bauxite and red muds are low (usually <1,000 ppm) compared with carbonatite deposits such as Mountain Pass and Mount Weld, which have grades of around 80,000 ppm REE (Wall, 2014). They are more comparable to those in lower grade Chinese ion-adsorption

clay deposits that usually contain 500-2,000 ppm REE (Kynicky *et al.,* 2012; Moldoveanu and Papangelakis, 2012). Heterogeneity and differences in the chemistry of bauxite and red mud make it difficult to develop a common REE leaching method that can extract 100% of REE from bauxite or its by-products. Currently, the focus of REE extraction is mainly on red mud as it has double the REE concentrations compared with the initial bauxite (Ochsenkühn-Petropoulou *et al.,* 1994). Various studies have achieved significant results towards this direction using acids (e.g. Ochsenkühn-Petropoulou *et al.,* 1996; Borra *et al.,* 2015; Gamaletsos *et al.,* 2016), but these still need more development in order to be economically feasible and able to be established as parts of aluminium's industry.

Table 1 - Leaching results for REE, showing the leached amounts of REE after using a protocol based on Sanematsu *et al.* (2013).

	Baux 1 (ppm)	Baux 1 Leachate (ppm)	Baux 1 REE % Leached	Baux 2 (ppm)	Baux 2 Leachate (ppm)	Baux 2 REE % Leached
La	26.70	9.31	34.88	58.80	16.01	27.22
Ce	404.20	56.82	14.06	384.80	221.84	57.65
Pr	13.01	5.24	40.28	11.68	4.25	36.41
Nd	55.80	21.09	37.80	40.70	15.36	37.74
Sm	13.91	5.55	39.91	7.99	3.26	40.81
Eu	3.01	1.07	35.48	1.74	0.61	35.31
Gd	12.88	4.19	32.55	9.47	2.96	31.21
Tb	1.80	0.48	26.91	1.42	0.38	27.03
Dy	9.68	2.27	23.46	9.16	2.18	23.84
Ho	1.85	0.34	18.44	1.87	0.37	19.72
Er	4.99	0.76	15.27	5.40	0.89	16.41
Tm	0.77	0.09	11.10	0.86	0.10	11.87
Yb	5.18	0.45	8.67	5.82	0.54	9.20
Lu	0.74	0.06	8.27	0.86	0.07	7.97
Y	44.60	6.52	14.62	53.20	9.50	17.86
ΣREE	599.12	114.25	19.07	593.77	278.32	46.87
ΣLREE	513.62	98.01	19.08	503.97	260.72	51.73
ΣHREE	85.50	16.24	18.99	89.80	17.60	19.60

Note: ΣREE are La-Lu and Y, LREE are La-Sm and HREE are Eu-Lu and Y (Wall, 2014)

Our preliminary results suggest that up to ~50 % of the total REE in bauxite (especially in the upper parts of the weathered profile) could be leached easily using ammonium sulphate (Table 1 and Figure 1). Consequently, leaching 100-300 ppm of REE directly from bauxite results in consuming fewer and cheaper reagents compared with red muds, where large amounts of strong acids and long digestion time periods are needed to leach high proportions (almost 80%) of REE (e.g Borra *et al.,* 2015). The high costs of acids needed for leaching as well as the low HREE contents of Greek red muds seem problematic for an economically feasible REE extraction. Moreover, the disposal of the acids used may have important environmental implications. The most important benefit of the suggested method is that it is less likely to interfere with the Bayer process because it may be easy to install and run in the plant at the point where bauxite is gathered, right before passing through the Bayer process.

The preliminary results presented in this study also indicate that the easily leachable REE in Greek bauxite, extracted using ammonium sulphate, may occur as ion-adsorbed phases, i.e. mainly as ions

adsorbed onto phases such as kaolinite, illite and chamosite, which are present in Greek bauxite (Tsirambides and Filippidis, 2012; Laskou and Economou-Eliopoulos, 2013). These REE phases will not be retained in the solid phase after the bauxite passes the Bayer process, due to the ore processing in a concentrated sodium hydroxide (NaOH) solution at various temperatures and pressures (Power *et al.,* 2011; Binnemans *et al.,* 2015). It is therefore likely that an ammonium sulphate leaching method may not be efficient in removing REE for red mud waste.

6. Conclusions

Our pilot study suggests that some amounts of REE could be leached in a simple and cheap way by taking advantage of some easily leachable REE phases occurring in bauxite. Even if those amounts are relatively small, application of this method could result in further income for Aluminium of Greece S.A., in addition to the induction of Greece and hence EU in the rare earth oxide (REO) production chain. However, further research focused on improved characterization of bauxite and red mud waste phases, selective mining of REE enriched bauxites, and the development of efficient REE recovery techniques from bauxites and red muds, is required to fully assess these potentially important resources.

7. Acknowledgements

8. References

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