RARE EARTH ELEMENTS IN KARST-BAUXITES: A NOVEL UNTAPPED EUROPEAN RESOURCE?

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Abstract

Karst-bauxite deposits form as a result of the accumulation of residual clay minerals in depressions on a karst limestone surface, and their subsequent lateritic weathering. Rare earth elements (REE) become concentrated in the bauxite deposits due to crystallisation of authigenic REE-bearing minerals, accumulation of residual phases and the adsorption of ions on clays and other mineral surfaces. REE are concentrated in the red mud waste generated by alumina production from bauxite through the Bayer process. Red muds thus contain on average 900 ppm REE compared with typical values of <100 ppm to ~500 ppm REE in the bauxites. Extraction of REE from red mud has been shown to be feasible although it is challenging due to the heterogeneous spatial distribution of REE in the bauxites and the need for development of appropriate processing methods. With annual European extraction of bauxite estimated to be approximately 3.5 million tonnes per annum, resulting in approximately 1.4 million tonnes of red mud from the production of alumina, understanding the REE resource potential of bauxites is integral to the assessment of European REE resources.

Introduction

Research into the rare earth element (REE) content of bauxites has a long history, with authigenic rare earth minerals first identified in the San Giovanni Rotondo deposit in Italy[1]. Further research by Maksimović and Pantó[2,3,4,5,6,7,8] in particular led to the discovery of authigenic REE in multiple deposits in the Balkans and Greece (for example at Marmara, Greece, Vlasenica, Bosnia and Herzegovina and Štitovo, Montenegro). Research into the potential of bauxites as a source of REE, Sc and Y has been undertaken by many researchers over the past forty years (e.g. [9,10,11,12,13,14,15]). This paper reviews this previous work to consider the REE resource potential of bauxites in Europe.

Bauxite is formed from the intense lateritic weathering of residual clays, which accumulate in topographic lows on continental surfaces. The two main classes of bauxites are: 1) those that form on aluminosilicate lithologies; and 2) those that form on limestone, known as karst bauxites[16], and which are the focus of this paper. Bauxite is the primary source for aluminium (Al) production globally and is relatively common in Europe, with deposits known from the majority of Mediterranean countries and intermittent exploitation occurring over many decades (Figure 1).
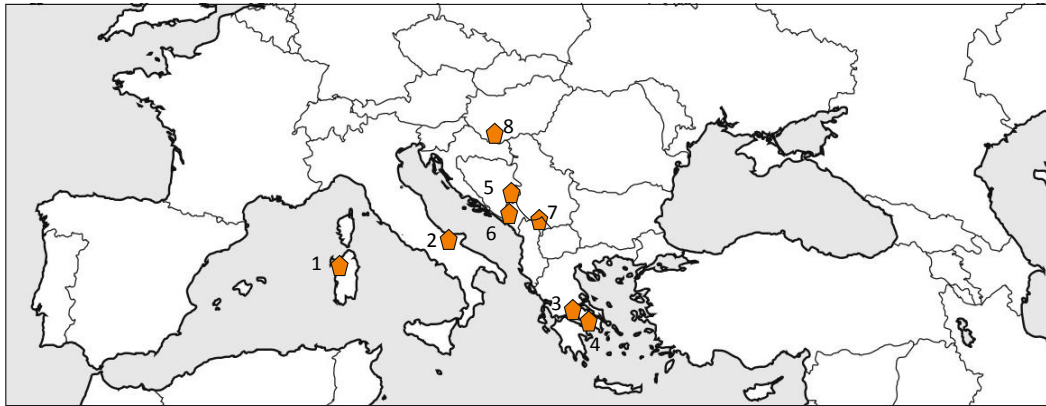

Figure 1: Map of southern Europe showing selected bauxite occurrences as mentioned in the text: Olmedo, Sardinia, Italy (1), San Giovanni Rotondo, Italy (2); Parnassos-Ghiona, Greece (3), Marmara, Greece (4); Vlasenica, Bosnia and Herzegovina (5); Štitovo pit, Nikšić, Montenegro (6); Grebnik, Kosovo (7); Nagyharsany, Transdanubian Central Range, Hungary (8).

Demand for REE is increasing, particularly for use in green energy technologies, e.g. wind turbines etc. As China currently dominates global production[17], there is increasing pressure to identify alternative European sources of these economically important metals. The growing demand for REE has recently been emphasised by numerous authors[18,19,20], and while recycling may contribute to meeting future demand, the separation of individual REE from recycled materials is very challenging with only 1 per cent of REE currently recycled from end-of-life products[19] (and references therein). There are currently no mines producing REE in Europe and although this is likely to change in the future, an alternative, readily available, source of REE would be attractive.

Red muds produced from alumina processing represents a potentially important concentration of REE as it has been shown that all of the REE pass through the alumina extraction process into the waste, and the total REE values are enriched by a factor of two from the original bauxite ore[11,13]. Currently red mud is viewed as waste

as it does not have any other purpose, although there have been attempts to find alternative uses for the material[21] (and references therein). .

Bauxite

Karst bauxite deposits are formed by accumulation of residual clays, derived from the weathering of aluminosilicate minerals[22], in depressions on carbonate palaeotopography. The contents of the depressions are bauxitised through deep lateritic weathering and desilicification of ferrilitic soils[23]. The conditions under which bauxitisation occurs are such that silica is incongruently dissolved from minerals such as feldspar and kaolin leaving an aluminium-rich residue[24]. Bardossy[16] distinguishes several subtypes: Kazachstonian type, Timan type, Ariège type, Tula type and Mediterranean type. These classifications are based on the composition of the deposits and the mode of karstification.
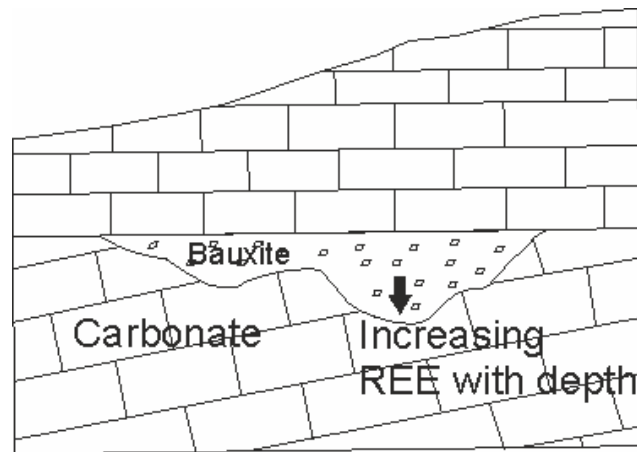

Figure 2: Schematic diagram showing the typical classic Mediterranean type karst bauxite (after Bardossy 1982[16]).

Mediterranean type karst bauxite deposits formed on both the European and Adriatic Mesozoic carbonate shelves in the Neotethys realm during the Mesozoic to Early Cenozoic[25,26]. Bauxitisation in this area occurred from the surface downwards leading to the ultimate loss of SiO_2 and Fe_2O_3 and accumulation of Al_2O_3 with depth[23]. This paper focuses on Mediterranean type karst bauxite.

Rare Earth Elements in Bauxite

Where REE are available to the weathering system, they can be adsorbed onto the surfaces of clay residues that form the bauxite deposit and are then concentrated with depth by bauxitisation[27,28]. With more intense bauxitisation there is a correlation with depth between both increased REE content and decreased silica content. Meteoric water can preferentially leach away silica produced from the dissolution of feldspar and kaolinite leaving an Al-rich residue[29]. However, the

process of REE concentration is dependent on multiple factors and is still poorly understood.

Authigenic rare earth element-bearing minerals

Where sufficient REE are available within the bauxite, bauxitisation has occurred *in situ* and where there has been no later transport or erosion of the deposit, authigenic REE-bearing minerals can form. REE are mobilised from the clay as waters percolate through the system during bauxitisation. As REE-bearing fluids descend through the deposit and reach the carbonate they become physically trapped allowing authigenic minerals to form where REE content is sufficiently high [27,28]; the most common is hydroxylbastnäsite-(Nd) (Nd(CO$_3$)(OH))[14,30]. In order for REE minerals to develop, the initial concentration of REE adsorbed onto the clay must be greater than about 1000 ppm[14]. If the initial concentration does not reach this threshold REE minerals are unlikely to form. Increases in REE content of up to almost six-fold have been recorded as a result of bauxitisation (e.g. at Nikšić, Montenegro and Grebnik, Kosovo[31] (and references therein)). Where the bauxites have been disturbed during formation REE can be lost from the system, such as in the karst-bauxite deposits in the Transdanubian Central Range in Hungary[32]. In Hungary reported REE concentrations vary greatly, ranging from ~81–~10 000 ppm. This is due to the detrital nature of some REE host minerals such as monazites sourced from the Mecsec mountains in the case of the Nagyharsany deposit, rather than authigenic mineral growth [9].

Conditions of mineral formation

Key parameters controlling the concentration of REE in bauxite include intensity of leaching by meteoric waters, pH, Fe content and the availability of ligands such as fluorine (F).

Water flow: Leaching of the bauxite by meteoric water can readily remobilise adsorbed REE[14]. The weathered limestone below the bauxite facilitates drainage and thus clay layers do not form within the bauxite, so the downward mobility of REE is not restricted[33,26].

pH: The alkaline nature of the underlying limestone creates a high pH that results in increased stability of REE-carbonate complexes (e.g.[34,35]). Stability increases with atomic number, allowing HREE to be preferentially retained in solution as carbonate ions[25]. The distribution of REE along this 'pH barrier' is heterogeneous and the REE can be concentrated in lenses or in micropores, space fillings and microveins[14].

Fe content: Fe-rich goethite has a significant scavenging effect, preferentially fixing mobile REE, in particular the LREE, within residual Fe-rich layers[36]. Positive correlations exist between Fe$_2$O$_3$ and ∑REE, particularly where Fe oxy-hydroxides occur as ferrigenous ooids (e.g. Olmedo Bauxite, Italy[25]).

F depletion: Bauxite is typically depleted in F; this depletion is a critical factor in controlling the type of minerals that form. F can be substituted by -OH groups to form hydroxylbastnäsites such as hydroxylbastnäsite-(Nd), which has been described from Nikšić in Montenegro. Hydroxylbastnäsites are the most common authigenic REE minerals found in bauxite[6].
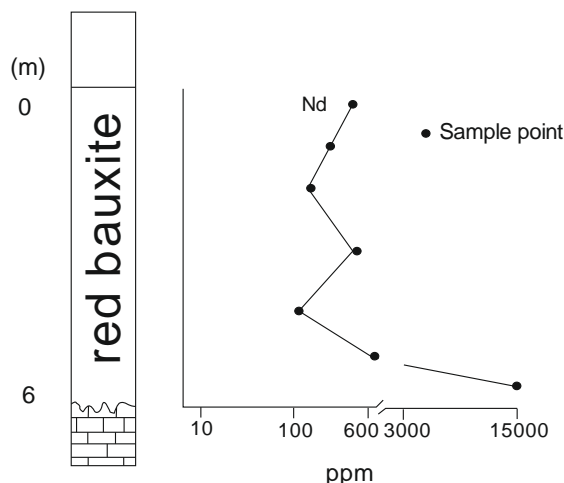

Figure 3: Typical Nd distribution through the Štitovo bauxite, Montenegro (after Maksimovic and Panto 1995 (figure10.1 chapter 10 p262)[14]). The enrichment of Nd at the base allows for the formation of authigenic REE minerals such as Nd-goyazite, bastnäsite and hydroxylbastnäsite-(Nd)[37,28].

Ce does not have the same *per descensum* correlation that is observed for the other REE. This is due to the oxidation of Ce^{2+} to Ce^{4+} in the strongly oxidising environment created during bauxitisation[28,38,39]. This can result in the skewed distribution of Ce within bauxite profiles with Ce enrichment occurring in the upper parts of the bauxite deposit whilst the rest of the REE have been transported downwards.

Rare Earth Elements in Red Mud

To separate alumina from bauxite, a processing route known as the Bayer process is employed. Bauxite is digested in a hot sodium hydroxide solution to convert the alumina to aluminium hydroxide, which dissolves in the hydroxide liquor. The other components of bauxite do not dissolve. The solution is clarified by filtering off the solid impurities, which forms the so-called bauxite residue or red mud. The actual composition of red mud depends on the type of bauxite, the mining location and the process parameters of the Bayer Process[40]. REE content in red mud has been shown to double as a result of the Bayer Process[11] and this is consistent in both Jamaican and Greek deposits[10]. Mineralogical studies have shown that in the Jamaican red mud samples the REE are dispersed as ion-adsorbed elements or as an unknown phase associated with iron oxides[41]. The resource potential of red muds in Europe

(including Turkey) is significant with approximately 3.5 million tonnes (Mt) of bauxite ore extracted in 2012[17], which resulted in the production of an estimated 1.4Mt of red mud waste.

Rare Earth Elements in Greek Bauxites

The karst-bauxite deposits of Greece are among the world's most important sources of bauxite. Exploitable deposits of bauxites exist mainly in the regions of Mt Parnassus, Mt Giona and Mt Helikon (central Greece) and reserves are approximately 600 000 t – the 9th largest bauxite reserves globally[42]. Previous research on these deposits includes the quantification of REE and Sc in bauxites and red mud waste[43,11], and development of separation techniques for Sc and REE from the red mud[12].

Parnassos-Ghiona bauxite

The Parnassos-Ghiona geotectonic zone is characterised by nearly continuous sedimentation of epicontinental reef-like carbonates from the Upper Triassic to the Upper Cretaceous. Bauxites occur in three main horizons (B1–B3) (Figure 4). Geochemical analysis of samples from this region has been conducted in this study and the results are presented below in Figure 5 and Table 1.

Eocene flysch overlain by Quaternary conglomerates

Upper Cretaceous limestone

B3 horizon

Lower Cretaceous limestone

B2 horizon

Upper Jurassic limestone

B1 Horizon

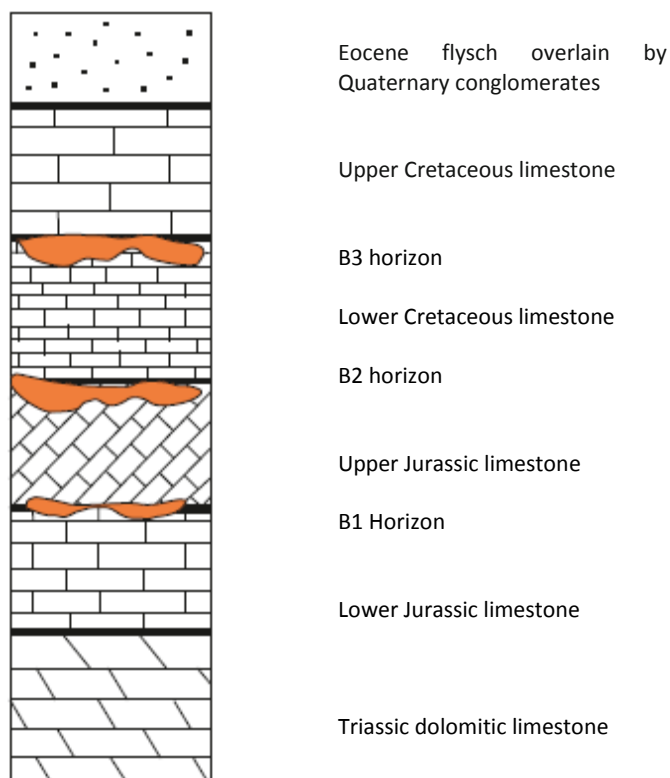Lower Jurassic limestone

Triassic dolomitic limestone

Figure 4: Stratigraphic column showing the three bauxite horizons (after Laskou and Economou-Eliopoulos, 2013)[50]
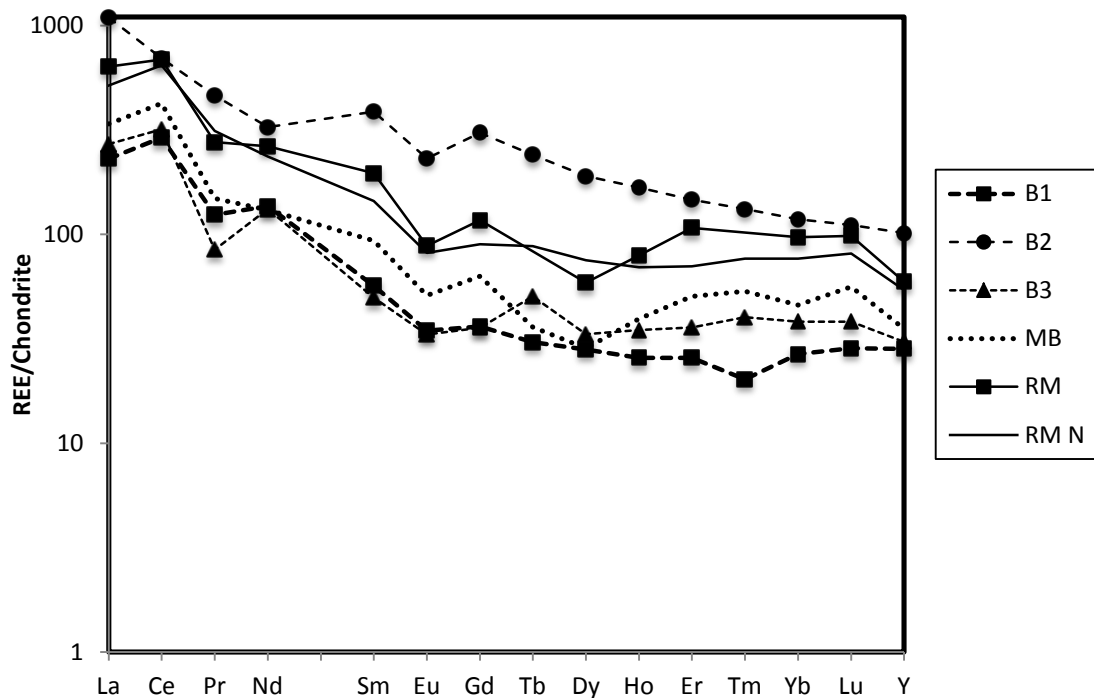
Figure 5: Plot of average published REE values for each of the three main horizons (B1–B3) and red mud (RM); and preliminary data based on 18 samples taken from three dehydrated red mud waste tips at the Aluminium S.A. site (RM N). Data for mixed bauxite ore (MB) that enters the plant is shown. All values are chondrite normalised using McDonough and Sun 1996[44]. [Data from[33,43,11,45,46,47,48,49,50]].

Tsirambides and Filippidis[53] report ΣREE values in the bauxites and lateritic bauxites of central Greece as 3275 to 6378 ppm. Although these values are significant, these concentrations are unlikely to be reflective of all Greek bauxite deposits. High values are likely to result from the sampling of localised areas with REE enrichment along the footwall limestone, and are not representative of average REE concentrations in the bauxite. Chondrite-normalised data for average REE values from the three different bauxite horizons of the Parnassos-Ghiona zone are shown in Figure 5. The combined REE values for bauxite horizons B2 and B3 (Figure 4) were estimated using samples of the mixed throughput ore from the plant at Aluminium S.A., Greece (sample MB). Data compiled for this study indicates an average ΣREE+Y value of ~500 ppm for the bauxite and ~900 ppm for the red mud samples (Table 1). REE concentrations in the collated data indicate variation across the three main bauxite horizons, with a mixture of these horizons entering the processing plant (MB). The two-fold increase in REE in the red muds compared with the original bauxites is consistent with the literature e.g.[11].

	B1 (ppm)	B2 (ppm)	B3 (ppm)	MB (ppm)	RM (ppm)	RM N (ppm)
Y	44.4	159.1	48.03	55.44	93.11	85.1
La	54.5	258.35	64.08	80.2	150.59	122.19
Ce	178	427.53	195	259.59	421.62	394.92
Pr	11.5	42.95	7.85	13.8	25.62	29.02
Nd	62.33	149.23	60.39	59.86	120.9	107.92
Sm	8.4	57.2	7.36	13.81	29.09	21.4
Eu	1.95	12.99	1.87	2.87	4.97	4.59
Gd	7.2	61	7.1	12.53	23.27	17.86
Tb	1.1	8.66	1.82	1.3		3.17
Dy	6.9	46.88	8.2	7	14.44	18.51
Ho	1.4	9.16	1.9	2.15	4.33	3.8
Er	4.1	23.46	5.74	8.07	17.2	11.24
Tm	0.5	3.27	0.99	1.32		1.89
Yb	4.3	19.01	6.14	7.4	15.6	12.33
Lu	0.7	2.73	0.94	1.38	2.42	1.99
∑REE+Y	387.28	1281.52	417.41	526.72	923.16	835.93

Table 1: REE values compiled from the literature for B1–3, RM and MB samples. New data is presented as RM N. Samples were analysed for ∑REE+Y content in the geochemical laboratories of the Camborne School of Mines.

The variation in REE concentration between specific horizons, particularly the enrichment observed in B2 is likely to be a function of sampling an enriched zone, which is not necessarily reflective of the entire horizon. The vertical, and probable lateral, variation in REE concentrations illustrate the need for a robust sampling strategy involving the collection of more carefully characterised samples.

Bauxite as a potential resource

Production of REE in the form of RE oxides (REO) is currently limited to six countries: Russia, USA, China, Brazil, Malaysia and Australia[17]. With total production of bauxite from Europe (+Turkey) of ~3.5 Mt[17], this results in annual production of ~1.4 Mt of waste red mud, with an average homogenised REE content of ~900 ppm, based on ∑REE+Y from sample RM in Table 1. If these quantities of red muds were processed and REE extracted, it would result in total REE production of ~1300 t annually. In a best case scenario, with REE enriched bauxite having an average ∑REE concentration of ~2000 ppm[14], this would result in REE production of a ~2800 t annually. This is based on REE extracted from the Bayer Process would likely be in the form of oxalates or carbonates, which have a relatively low market value as additional costs are incurred in separating the individual REEs. In Greece, Aluminium S.A. is the

largest consumer of Greek bauxite, processing over 1.5 Mt annually and producing 700 000 t of red mud waste annually[51,52]. Deposition of dehydrated waste mud started in 2009. Accordingly the total volume accumulated is approximately 3.5 Mt. Assuming an average ΣREE of 1000 ppm, if processed this could potentially produce ~3500 t of contained REE. It is notable that the data also show a relatively high content of HREE relative to LREE, which may have economic implications. However, there are challenges associated with the exploitation of red mud waste, specifically the difficulty in controlling REE concentrations. REE concentration varies significantly between deposits and within individual bauxite horizons and this directly affects the REE concentration of the resulting red muds.

Discussion

Fully understanding the mineralogy and natural processes of REE enrichment in bauxites is vital to assessing the REE resource potential of bauxites and red muds in Europe. Great variability in both the mineral concentration and composition between and along bauxite horizons is documented[14]. This means acquiring red muds with consistent REE concentrations to feed a processing plant would be challenging. However, there are occurrences which are more enriched in particular REE, such as the Montenegro deposits at Niksic, which host hydroxylbastnäsite-(Nd) as the predominant REE mineral. Improved understanding of the heterogeneity of REE distribution within the bauxite could allow for the targeting of REE enriched portions of the bauxite. It is likely that once the supply of REE becomes more geographically diverse there will be greater emphasis on acquiring metals from sources with the lowest environmental impact[19]. Existing stockpiles of red muds could represent a more environmentally sustainable source of REE for Europe as additional mining is not necessary and current "stockpiles" of red mud would be viewed as a resource rather than a waste product with the associated disposal issues.

Although the quantities of REE contained in red muds appear to be low (average ~900 ppm) when compared with primary deposits of carbonatite (e.g. Mountain Pass and Mount Weld have grades of about 80 000 ppm REE[19]), in a scenario based upon a REE grade of 2000 ppm (~2800 t contained REE) red muds could account for about 10 per cent of EU demand for REE. EU imports of rare earths in 2011 (REE+Y+Sc metals and compounds) totalled ~26 500 t[54].

More significantly, it may contribute to improving security of supply for some REE to the European market. European production of REE in high demand would ensure a secure supply source and remove some of the risks associated with the importation of REE from geopolitically unstable countries.

The economic viability of REE production from European red muds needs careful assessment due to the investment required in mineral processing and extraction technology. Further research focused on improved characterisation of red mud

stockpiles, selective mining of REE enriched bauxites, and the development of efficient REE recovery techniques from red muds is required to fully assess these potentially important resources.

Acknowledgments

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