A review of the potential for rare earth element resources from European red muds: examples from Seydişehir, Turkey and Parnassus-Giona, Greece

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Abstract

Rare earth elements (REE) are viewed as 'critical metals' due to a complex array of production and political issues, most notably a near monopoly in supply from China. Red mud, the waste product of the Bayer process that produces alumina from bauxite, represents a potential secondary resource of REE. Karst-bauxite deposits represent the ideal source material for REE-enriched red mud as the conditions during formation of the bauxite allow for the retention of REE. The REE pass through the Bayer Process and are concentrated in the waste material. Millions of tonnes of red mud are currently stockpiled in onshore storage facilities across Europe, representing a potential REE resource. Red mud from two case study sites,

one in Greece and the other in Turkey, has been found to contain an average of approximately 1000 ppm total REE, with an enrichment of light over heavy REE. Although this is relatively low grade when compared with typical primary REE deposits (Mountain Pass and Mount Weld up to 80000ppm), it is of interest because of the large volumes available, the cost benefits of reprocessing waste, and the low proportion of contained radioactive elements. This work shows that around 12000 tonnes of REE exist in red mud at the two case study areas alone, with much larger resources existing across Europe as a whole.

Introduction

Processing of the primary aluminium ore, bauxite, to produce alumina (Al_2O_3) using the Bayer process produces a waste material known as red mud. Long term storage of this is expensive and represents an environmental risk, as demonstrated by disasters such as the red mud dam failure at Kolontár, Hungary which caused extensive damage to neighbouring land and waterways and the death of nine people (Gelencsér *et al*., 2011; Milačič *et al*., 2012; Anton *et al*., 2014). To mitigate this risk, as well as to reduce cost, a number of studies have been undertaken to identify possible uses for red mud (e.g. Klauber *et al*., 2011; Power *et al*., 2011; Binnemans *et al*., 2013a).

Annual global extraction of bauxite in 2013 (the last year for which figures are available) was approximately 296 million tonnes (Mt), up 16% from 2012 (BGS, 2015). Annually, this results in the production of approximately 150 Mt of red mud

(IAI, 2014). Decades of work on the valorisation of red muds have not yet found a significant alternative use for this voluminous waste product (Klauber *et al*., 2011). Only around 2 Mt (~1.6% of the global total) is currently used each year (Ritter, 2014), mostly in construction materials, as cement additives and in brick making (Klauber *et al*., 2011).

The Bayer process produces virtually pure alumina (> 99% Al_2O_3) and therefore almost all non-alumina 'impurities' from the original bauxite end up in the red mud waste. These 'impurities' have been found to include significant amounts of gallium, scandium and REE (Ochsenkühn-Petropoulou *et al.,* 1995, 1996; Smirnov and Molchanova, 1997; Akcil *et al*., 2013; Rusal, 2014; Borra *et al*., 2015). Ga and the REE are classed as 'critical metals' (EC, 2014) i.e. those having limited global distribution of production, no known substitutes, highly specialised applications and being of economic significance (Graedel *et al*., 2014).

REE are generally divided into light REE (LREE) from lanthanum to samarium and heavy REE (HREE) from europium to lutetium; Yttrium behaves as a HREE due to its similar physical and chemical properties (Wall, 2014). HREE, followed by LREE, are classified by the European Commission (EC, 2014) and British Geological Survey (BGS, 2012) as the most 'critical' of all raw materials. They are deemed essential to the economies of Canada, Japan and the US among others (CREEN, 2013; Humphries, 2013; Mitsubishi Electric, 2014). Annual global production of REE (expressed as rare earth oxides (REO)), was approximately 100 170 t in 2013 (BGS,

66 2015). Of this, over 90% was supplied by China. This geospatial concentration of
67 production has raised concerns over security of supply (Hatch, 2012).

68 The REE are now essential to many green and modern technologies such as smart-
69 phone screens, electric cars and wind turbines (Wall, 2014). This has led to
70 increasing global demand for REE with demand growth of 5.6% between 1970 and
71 2010 (Alonso *et al*., 2012). Present development of electric vehicles and wind
72 turbines relies heavily on dysprosium and neodymium for rare-earth magnets.
73 Future adoption of these technologies may result in large and disproportionate
74 increases in the demand for these two elements (Alonso *et al*., 2012). Economic
75 exploitation of REE from primary deposits, such as alkaline magmatic rocks,
76 carbonatites and ion adsorption clays, is dependent on the ratio of LREE to HREE in
77 the deposit and metallurgical characteristics of the REE present (Simandl, 2014).
78 Alternative sources of REE are becoming more important due to a range of factors
79 including increasing demand, a poorly developed REE recycling industry (Simandl,
80 2014), a more volatile supply chain from China (Hatch, 2012), and the 'balance
81 problem', where demand for specific elements and the natural abundance of those
82 elements in deposits are 'unbalanced', resulting in excess supply of less in-demand
83 REE (Binnemans *et al*., 2013b; Binnemans and Jones, 2015). In the European Union
84 (EU) this has led to the seventh framework programme (FP7) funding of the EURARE
85 (European Rare Earth Resources, www.eurare.eu) project which aims to research
86 and develop European resources and production of REE in a sustainable,
87 economically viable and environmentally friendly way. Europe in this context refers

88 to the EU-28, Liechtenstein, Iceland, Norway and Switzerland, and the candidate
89 and potential candidate countries. Russia and Ukraine are not included in this work.

90 Primary resources of REE have been identified and explored across Europe over the
91 past decades (Goodenough *et al*., 2016), such as at Norra Kärr, Sweden; Fen,
92 Norway; the Kvanefjeld and Kringlerne deposits in Greenland; and the Aksu Diamas
93 deposit in Turkey. However, none have so far gone into production. Attention has
94 also turned to secondary sources, mainly from the recycling or processing of waste
95 materials. Europe's red muds represent one such possible resource. The work
96 presented here aims to assess the REE potential of European red muds. The study
97 is based on two case examples, Seydişehir, Turkey and Parnassus-Giona, Greece,
98 where the parent karst-bauxites have been identified as REE-bearing (Ochsenkühn-
99 Petropoulou *et al.,* 1991; Laskou and Andreou, 2003; Karadağ *et al*., 2009), and the
100 red muds are stored in accessible 'dry' piles or tailing ponds. These case studies are
101 put in the context of a review of European red mud resources where resource
102 estimates of available REE in European red mud storage facilities are presented.

103 **Bauxites and alumina in Europe**

104 Within Europe, bauxite is currently extracted in six countries: Bosnia and
105 Herzegovina, France, Greece, Hungary, Montenegro and Turkey. Production in
106 2013 equalled almost 3.5 Mt, approximately 1% of global production (BGS, 2015).
107 Historically, bauxite has been exploited more widely across Europe, particularly in
108 the Mediterranean region (Figure 1), representing a significant proportion of global
109 bauxite production (~15% in 1974 (IGS, 1978)). There are three main categories of

bauxite deposit (Bárdossy, 1982): 1. Lateritic bauxite deposits, which derive from *in situ* weathering of aluminosilicate rocks; 2. Karst bauxite deposits, which occur in the karst topography of limestone and dolomite and comprise aluminosilicate residues that have been transported from either proximal or distal locations; 3. Tikhvin-type deposits, which are laid down on aluminosilicate rocks but have no genetic relationship to them. Karst bauxite deposits can be subdivided further into six main types (Bárdossy, 1982; Bosák *et al*., 1989), of which the 'Mediterranean type' karst bauxite deposits are of the most interest in Europe due to the amount of REE present. Red mud waste from these Mediterranean bauxite types is the focus of this paper.

Formation of karst bauxites begins with muddy sediments being washed into hollows in karst topography. These sediments are subsequently bauxitised through deep lateritic weathering. Bauxitisation is facilitated by moderate temperatures and through-put of mildly alkaline fluids, which allow silica to be incongruently dissolved from minerals such as feldspar and kaolinite leaving an aluminium-rich residue (Gow and Lozej, 1993; Bland and Rolls, 1998). Alongside this, Al may accumulate from a variety of sources including the insoluble residue of limestone, other aluminosilicate material (volcanic ash and clay layers) within the limestone, or the erosion, transportation and weathering of aluminosilicate rocks. The main Al-bearing minerals in bauxite are the monohydrates boehmite ((γ-AlO(OH)) and diaspore ((α-AlO(OH)), and the trihydrate gibbsite ($Al(OH)_3$). The main gangue minerals include hematite (Fe_2O_3), goethite (FeO(OH)), anatase (TiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$) and minor quartz (SiO_2).

133 The process of bauxitisation progresses from the top downwards and laterally
134 outward following the direction of drainage (Bárdossy, 1982). Karst-bauxite
135 typically forms under moderate temperatures in subtropical climates usually with
136 an average mean temperature of 26°C (Bárdossy, 1979). Good drainage of slightly
137 alkaline fluids through the developing bauxite is essential for formation. It has been
138 shown that the major element chemical composition of bauxites varies from one
139 region to another and within individual deposits (Akinic and Artir, 2008). The
140 formation conditions also have an important influence on the REE content and
141 distribution within the bauxite. The sources and formation conditions of selected
142 European karst-bauxite deposits, and the implications that these may have for REE
143 content, are discussed below. The size and grade of bauxite deposits is dependent
144 on the duration of the weathering (Bogatyrev *et al*., 2009), but the effect of the
145 duration of weathering on the REE content is unclear.

146 Alumina production from bauxite has been on-going in Europe since the
147 development of the Bayer process over 125 years ago. To separate alumina from
148 bauxite, the ore is digested in a hot sodium hydroxide solution to convert the
149 alumina to aluminium hydroxide, which dissolves in the hydroxide liquor. The other
150 components of bauxite do not dissolve. The solution is clarified by filtering off the
151 solid impurities, which forms the bauxite residue or red mud (Hind *et al*., 1999). The
152 composition of red muds depends on the nature of the parent bauxite, the mining
153 location and the parameters of the Bayer process (Hind *et al*., 1999).
154 Mineralogically, red mud is mainly composed of red coloured iron oxides in the
155 form of hematite (Fe_2O_3) and maghemite (γ-Fe_2O_3), aluminium oxides in the form

156 of diaspore (α-AlO(OH)) and gibbsite ($Al(OH)_3$), and silicon, calcium, sodium and
157 titanium oxides such as calcite ($CaCO_3$), silicon calcium aluminate hydroxide
158 ($Ca_3Al_2(SiO_4)(OH)_8$), perovskite ($CaTiO_3$), rutile (TiO_2) and cancrinite
159 ($Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2.2H_2O$ (Atasoy, 2007). Red muds typically have a density of
160 around 2.75 g/cm^3 and a pH of > 12.

161 Red muds are produced at a rate of approximately 150 Mt per year globally. There
162 are now approximately 60 alumina refineries worldwide outside China using the
163 Bayer process, of which 10 are located in Europe (Figure 2). An additional 49
164 refineries were operating in China in 2011 (IAI, 2014). European refineries produce
165 alumina from both European and imported bauxite in order to supply the needs of
166 the European market. The importation of bauxite from a wide range of sources
167 makes it difficult to assess the REE content of the resulting red mud waste. In
168 Europe, the largest alumina refinery is Aughinish in the Republic of Ireland, which
169 has an output of 1.93 Mt of alumina per annum. Each tonne of alumina produced
170 results in the formation of between 0.7 and 2 tonnes of red mud (IAI, 2014).
171 Assuming an average overall ratio of 1:1.5 alumina to red mud (Hamada, 1986;
172 Power *et al*., 2011), the Aughinish plant is likely to produce almost 3 Mt of red mud
173 per annum.

174 Worldwide, an estimated 2.7 billion tonnes (Bt) of red muds have been produced
175 since the development of the Bayer process (Power *et al*., 2011). These have been
176 treated in a variety of ways, including storage in onshore lagoons and direct marine
177 disposal (Power *et al*., 2011). Historically, large quantities of the waste material

were directly dumped into the sea, however, this practice has been regulated under the 'Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (IMO, 1972)', the 'London Convention' for short. The practice of disposal at sea is expected to be completely abandoned by 2016 (IAI, 2014). Most commonly, red muds are stored in settling ponds onshore in closed cycle disposal systems; no alumina refineries built after 1970 are known to employ marine disposal of red muds (Power *et al*., 2011).

Statistics on European alumina production since 1972 have been gathered from the British Geological Survey's World mineral statistics database and are shown in Figure 3. Greek production before 2009 is not included, as before then red muds were disposed of at sea. The quantities of red muds likely to have been produced annually in Europe and stored onshore since the introduction of the 'London Convention' have been estimated as at least 200 000 t, using a minimum ratio of 1:0.7 tonnes of alumina to residue and a maximum ratio of 1:2 tonnes of alumina to residue, with an average ratio of 1:1.5 tonnes of alumina used (Figure 3).

Rare earth elements in bauxite

The characterisation of REE-containing minerals in bauxites was pioneered in the 1970s (Bárdossy and Pantó, 1973; Maksimović and Roaldset, 1976; Maksimović and Pantó, 1978; Vukotić, 1983). Of historical note was the first identification of secondary minerals of the bastnäsite group in the San Giovanni Rotondo bauxite in Italy (Bárdossy and Pantó, 1973). Since then, both authigenic and detrital REE-bearing minerals have been found in bauxites. The most common authigenic REE-

200 bearing mineral is hydroxylbastnäsite-(Nd) ($Nd(CO_3)(OH)$), while monazite
201 ($(Ce,La,Nd,Th)PO_4$) is the most common detrital REE-bearing mineral (Maksimović
202 and Pantó, 1996). In some occurrences the presence of detrital minerals can result
203 in high REE values, e.g. at Nagyharsány, a Hungarian monazite-bearing bauxite
204 which has total REE (*TREE*) of up to 10000 ppm (Bárdossy *et al*., 1976). The leaching
205 of monazite in this deposit led to the precipitation of authigenic bastnäsite-group
206 minerals near the base of the bauxite (Bárdossy *et al*., 1976; Maksimović and Pantó,
207 1996). In an example from the Southern Apennines of Italy, detrital monazite,
208 xenotime (YPO_4), and supergene LREE-enriched phosphates (high Ce, low La-Nd,
209 Ca minerals and florencite-type ($(REE)Al_3(PO_4)_2(OH)_6$) minerals) derived from the
210 weathering of monazite were detected in bauxite using SEM-EDS and QEMSCAN®
211 (Mondillo *et al*., 2011; Boni *et al*., 2013). In addition, bauxites from the Southern
212 Appenines (Italy) (Boni *et al*., 2013) and Nurra (Sardinia) (Mameli *et al*., 2007)
213 contain authigenic high-Ce, Ca-bearing fluorcarbonate minerals ($REE_2Ca(CO_3)_3F_2$).
214 Parisite ($Ca(Ce,La)_2(CO_3)_3F_2$) has previously been identified in the basal parts of the
215 Spinazzola bauxite in Italy (Mongelli, 1997; Mongelli and Acquafredda, 1999),
216 however, recent analysis suggests that parisite occurs homogeneously throughout
217 the deposit (Mongelli *et al*., 2014).

218 Fractionation of LREE and HREE has been noted in many Mediterranean bauxites
219 (Maksimović and Pantó, 1991; Mongelli, 1997; Laskou and Economou-Eliopoulos,
220 2007; Karadağ *et al*., 2009; Boni *et al*., 2013), resulting in vertical separation of REE
221 in bauxite profiles (Boni *et al*., 2013). Fractionation of Ce, which behaves differently
222 to the other REE, in particular in the uppermost parts of bauxite, is as a result of the

supergene oxidation of Ce^{+3} to Ce^{+4}. This allows precipitation of cerianite ($(Ce^{4+},Th)O_2$) to occur, with resultant Ce-depleted fluids percolating through the system. Scavenging by iron oxide phases, such as goethite (Boni *et al*., 2013), of Ce-depleted fluids results in further fractionation of REE between the ooids (concentric particles of bauxite with a diameter of between 100 and 1000 μm (Bárdossy, 1982)) and matrix of the bauxite in basal parts of the bauxite (Mongelli, 1997). Subsequent dissolution of cerianite under acidic conditions and *per descensum* transport of REE can result in the precipitation of LREE-rich minerals, such as parisite, at the base of the deposit (Mongelli, 1997; Mameli *et al*., 2007). Parisite in particular precipitates under alkaline conditions, such as those found at the base of the bauxite due to the alkaline aquifers in the underlying limestone. Parisite precipitation throughout a bauxite deposits, such as in the Spinazzola bauxite, can be explained by cyclical changes in water table levels and subsequent changes in Eh and pH (Mongelli *et al*., 2014).

Preferential uptake of REE by both iron and manganese mineral phases has been identified in other systems such as in marine ferromanganese deposits (Ohta and Kawabe, 2001) and in river estuary systems where iron oxyhydroxide adsorption of LREE in particular occurs (Marmolejo-Rodríguez *et al*., 2007). The alkaline 'pH barrier' created by the underlying limestone aquifer influences the stability of the REE-carbonate complexes that form at the base of the deposit (Johannesson *et al*., 1995, 1996). As the stability of these complexes increases with atomic number, the HREE are preferentially retained in solution as carbonate complexes. The distribution of the REE along this 'pH barrier' is heterogeneous and they can be

246 concentrated in lenses and micropores, space fillings and microveins (Maksimović
247 and Pantó, 1996).

248 **Rare earth elements in red muds**

249 REE are concentrated into red muds through the Bayer process (Wagh and Pinnock,
250 1987) which results from the association of REE with iron and titanium phases
251 which pass through unchanged (Derevyankin *et al*., 1981). To illustrate this, red
252 muds from lateritic-type Timan bauxites in Russia have been shown to contain up
253 to 90% of the Nb, Sc and REE present in the original bauxite (Klyucharev *et al*.,
254 2013). Similarly, Ochsenkühn-Petropoulou *et al*. (1994) and Wagh and Pinnock
255 (1987) have demonstrated up to two-fold increases in REE, including Sc and Y, in
256 red muds when compared to the bulk chemistry of the Greek and Jamaican source
257 bauxites, respectively.

258 The minerals known to occur in red muds include some that are produced during
259 the Bayer process, e.g. desilicification products such as sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$),
260 cancrinite ($Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2.2H_2O$) and Na-aluminosilicate, and calcite (Atasoy,
261 2007). However, most minerals are unaltered residual phases from the original
262 bauxite such as monazite, bastnäsite, hematite (Fe_2O_3), diaspore ((α-AlO(OH)),
263 gibbsite ($Al(OH)_3$) and quartz (SiO_2)(Power *et al*., 2011).

264 The mineralogy and petrology of REE-bearing minerals in red muds are relatively
265 poorly constrained (Ochsenkühn-Petropoulou *et al*., 1996; Borra *et al*., 2015).
266 Scavenging of REE by iron oxyhydroxides is observed in bauxites (Mongelli, 1997;

267 Mongelli and Acquafredda, 1999; Boni *et al*., 2013), however, the distribution of
268 REE phases in red muds is less well understood. An association between REE and
269 Sc with iron oxides in red muds has been observed through leaching studies (Borra
270 *et al*., 2015 and references therein). Sc is heterogenously distributed through the
271 red muds, being mainly contained within detrital mineral phases, such as the Sc-
272 enriched zircons found in bauxite (Boni *et al*., 2013). It may also either be adsorbed
273 onto the surface of iron oxide phases or enriched in the outer layers of iron oxide
274 particles (Borra *et al*., 2015), which may be the same in the case of REE.

275 The Bayer process involves many steps that affect the characteristics of the red
276 muds and hence potentially the REE distribution within the residue. Milling of the
277 bauxite ore initially changes the particle size and surface area of the minerals, which
278 has an impact on the settling rates within the red mud lagoons, and can also affect
279 chemical properties such as adsorption and dissolution of minerals. It is not possible
280 to apply a general enrichment factor for REE to red muds; it is necessary to
281 investigate the REE enrichment in each red mud locality and compare this, where
282 possible, with the parent bauxite. Further work to define the distribution of REE
283 within red muds is necessary in order to develop a clearer understanding of both
284 the distribution of REE and the phases that host REE within red muds.

285 Recent advances in the valorisation of red muds for minor metals include the
286 development of Rusal's pilot plant in the Urals, Russia, which is capable of
287 producing 2.5 t/a primary scandium oxide concentrate (RUSAL, 2014). Binnemans
288 *et al*. (2013a) give an overview of current methods of REE extraction from red muds.

289 Bench scale extraction of REE from dehydrated red muds using imidazolium-based
290 ionic liquids is being researched through the EURARE project at National Technical
291 University of Athens (NTUA) (Bourbos *et al*., 2014; Davris *et al*., 2014) while
292 leaching experiments are on-going at KU Leuven, Belgium (Borra *et al*., 2015). The
293 commercial extraction of REE from red muds has been further advanced by the
294 granting of a patent in both Canada and the US to Orbite Aluminae for the 'Orbite
295 Process', (Patent No. 14/371,364, Orbite, 2015), which uses red muds as a
296 feedstock for a new beneficiation stream that aims to extract REE and other minor
297 metals along with alumina, magnesium oxide and titanium dioxide from the
298 residue. It is thus clear that red muds have the potential to be a source for REE for
299 the European economy.

300 **European red muds, case studies**

301 The Mediterranean region has a complex geological history shaped most recently
302 by the closure of the Lower Palaeozoic to Cenozoic Palaeotethys and Neotethys
303 oceanic system which existed between the continents of Eurasia and Gondwana
304 (Robertson and Mountrakis, 2006). Continental collision resulted in the formation
305 of the Dinarides-Hellenides-Taurides orogenic belt, which extends across the
306 Eastern Mediterranean region, and which includes many carbonate units that
307 provide the karst topography in which karst bauxites have formed. The regional
308 geology is summarised below briefly to set the geological context for the bauxite
309 precursors of the case study localities.

310 **Sampling and analytical methodology**

311 Four samples of red muds (14/T/15-19) were collected at a depth of approximately
312 20 cm from different locations within the waste ponds at the ETİ Alüminyum S.A.
313 processing plant in Seydişehir, Turkey (inset Figure 4). The samples comprised 300
314 g of wet red muds; each individual sample consisted of three subsamples, which
315 were later recombined and dried. Preparation and analysis of the samples was
316 carried out at the British Geological Survey, Keyworth, Nottingham. Samples were
317 fused with sodium peroxide and 0.2 g of the resulting glass digested with dilute HCl
318 acid and then, HF acid. Dilute sample solutions (in 1% HNO_3+ 0.5% HCL) were then
319 analysed for 56 trace elements in an Agilent 7500CX series ICP-MS. Data for a
320 duplicate analysis of sample 14/T/16, for all elements, were within 0.18%. Data for
321 international standards (AGV-2 (andesite produced by USGS), BCR-2 (Columbia
322 River Basalt produced by USGS) and JR-2 (produced by Geological Survey of Japan))
323 were always within 6% of published values.

324 Samples of Greek red muds were collected from dewatered stockpiles at the
325 Aluminium S.A. alumina refinery in Agios Nikolaos. Three samples, equating to
326 approximately 5 kg in total, were taken at three different locations (13/Gr/A,
327 13/Gr/B and 13/Gr/Z) across the area of the stockpiled residue. Each of the samples
328 represent red mud residue from different deposits, mined at different times.
329 Preparation of the samples was carried out at the Camborne School of Mines,
330 Penryn, Cornwall. Five grams of each sample were analysed for 31 trace elements
331 (LF100 analysis) by ICP-MS, following lithium borate fusions at Bureau Veritas
332 Minerals Laboratories (BVML), Canada. International standards, BX-N bauxite
333 (reference material produced by ANRT (Association Nationale de la Recherche

Technique)) and STD SO-18 were used by BVML. Values obtained were within 2.7% of published values. Data from blank samples were checked for contamination and detection limits. Duplicate analyses (n = 1) of, sample 13/Gr/B were within ± 0.5%. Results are presented in Table 1, see supplemental data for duplicate, corrections and certified reference material data.

Case studies: red muds from Seydişehir, Turkey and Parnassus-Giona, Greece

Case study one: red muds from Seydişehir, Turkey

Geology

The Anatolide-Tauride terrane is one of three main terranes into which Turkey is subdivided (Şengör and Yılmaz, 1981). The terrane shows Gondwana affinities but was separated from the main mass of Gondwana by the southern branch of Neo-Tethys in the Triassic. Upper Triassic to Upper Cretaceous carbonate deposition formed several thousand metres of thick shallow marine carbonate deposits on a passive margin (Okay, 2008), which have subsequently been overthrust by Upper Cretaceous limestone and ophiolitic material. The karst topography formed on the carbonates in this region hosts a large number of bauxite, Al-laterite and manganese deposits which are mainly Upper Cretaceous to Cenozoic in age. The Mortaş and Doğankuzu Mediterranean-type karst bauxites are located in the central Tauride Mountains, close to Seydişehir, and are hosted in fossiliferous limestones of the Upper Cretaceous Mortaş Formation (Figure 4) (Temur *et al.*, 2009).

355 Both the Doğankuzu and Mortaş bauxites are mined to provide feedstock for the
356 alumina refinery at Seydişehir. The Mortaş deposit is lens shaped, 950 m in length
357 and 350 m wide, and the adjacent Doğankuzu bauxite elongate, with a strike length
358 of approximately 900 m and a width of 50 m (Karadağ *et al*., 2009). The deposits
359 occur between 1500 and 2000 m above sea level. The bauxites can be subdivided
360 into four horizons: massive bauxite, oolitic bauxite, breccia-bearing bauxite and
361 earthy bauxite. The main Al-bearing mineral is boehmite, with minor diaspore and
362 anatase, while the main accessory minerals are hematite, kaolinite and goethite.
363 REE are most enriched in the massive and oolitic bauxite horizons relative to the
364 hosting limestone (Karadağ *et al*., 2009). Bauxite deposition is thought to have
365 resulted from mass flow triggered by tectonic activity with transport of weathered
366 'bauxitic soil' over short distances into depressions and sinkholes in the limestone
367 (Öztürk *et al*., 2002). The bauxite deposits are between 1 and 40 m thick, and are
368 overlain by thin layers of claystone and argillaceous limestone. These are in turn
369 overlain by c. 50 m of Santonian massive limestone, with an overlying thick cover
370 of bioclastic limestone of Upper Cretaceous age and Eocene limestone and flysch.
371 The bauxites therefore must have formed in a depositional hiatus during the Upper
372 Cretaceous (Öztürk *et al*., 2002).

373 *Bauxite deposits and red muds*

374 The Seydişehir bauxite deposits of Mortaş and Doğankuzu have a total
375 resource of 26.3 Mt high-alumina boehmite bauxite at 55–67% Al_2O_3, of which
376 approximately 6 Mt had been mined by 2002 (Öztürk *et al*., 2002; Horkel, 2010).

These, the two largest bauxite open pits in Turkey, supply the only aluminium smelter in the country (Horkel, 2010), currently operated by ETi Alüminyum. Bauxite is mined from April to October annually and stockpiled at their plant in Seydişehir; extraction during the winter is suspended due to the inclement weather in the mountains. The extracted bauxite from the two mines is blended to create a plant feed with aluminium content suitable for processing at Seydişehir. Annual production is approximately 800 000 t of bauxite (BGS, 2015), generating approximately 1.5 Mt of red mud. Approximately 10 Mt are stockpiled in the tailing ponds. The red muds collected in the tailing ponds are waste material from both bauxite pits. It is not therefore possible to determine the relative contribution of REE from each of the deposits to the red mud samples.

Case study two: red muds from Parnassus-Giona, Greece

Geology

Greece is geologically subdivided into several tectonic zones, representing an amalgamation of terranes accreted over an extended period from the Lower Palaeozoic to the Mesozoic. The External Hellenides resulted from the Early Tertiary destruction of a Neotethyan oceanic strand known as the Pindos Ocean, which led to the collision between the Apulian and Pelagonian microcontinents (Doutsos *et al*., 2006 and references therein). The Parnassus-Giona zone is located within the External Hellenides, which is limited to Central Greece and consists almost entirely of limestone and dolomite of Mesozoic age (Doutsos *et al*., 2006).

The Parnassus-Giona tectonic zone is characterised by a nearly continuous sequence of Upper Triassic to Upper Cretaceous epicontinental reef-like carbonates. At the time of formation the Parnassus-Giona zone was a shallow lagoon, with both freshwater and seawater ingress due to changing tectonic and climatic conditions (Valeton *et al.*, 1987). Several phases of uplift, with associated marine transgressions and regressions, permitted the creation of multiple bauxite horizons during the Jurassic and Cretaceous. The materials which formed the bauxites in this area are thought to have been transported by sedimentary processes over a calcareous terrain for a distance of over 30 km (Petrascheck, 1989). The bauxite horizons, termed B1-B3, from oldest to youngest, formed during the Upper Jurassic to Middle Cretaceous (Figure 5) (Valeton *et al*., 1987, Laskou *et al*., 2010). These bauxite deposits comprise lenses, pockets and irregular masses. The economically most important deposits occur in the B3 horizon which is laterally extensive as a continuous layer with a thickness of between one and ten metres (Petrascheck and Mack, 1978; Valeton *et al*., 1987; Melfos and Voudouris, 2012; Tsirambides and Filippidis, 2012; Laskou and Economou-Eliopoulos, 2013). REE-bearing minerals occur in very small concentrations within the bauxites (Valeton *et al*., 1987). The mineral grains are small (between 1 and 10 μm) and can be authigenic, detrital, or material from weathered parent lithologies (Bárdossy *et al*., 1976). LREE-bearing minerals include phosphates, such as detrital rhabdophane-(Ce) ($(Ce,La)PO_4{\cdot}(H_2O)$) and florencite-(Ce) ($CeAl_3(PO_4)_2(OH)_6$), whereas HREE-bearing minerals are Y-phosphates such as detrital churchite ($YPO_4.2(H_2O)$) and xenotime (Laskou and Andreou, 2003). Monazite and secondary bastnäsite-group

minerals, such as hydroxylbastnäsite-(Nd) and hydroxylbastnäsite-(La) ((La)CO_3(OH,F)), and parisite-group minerals occur as micropore and fissure filling aggregates (Lymperopoulou, 1996; Maksimović and Pantó, 1996; Gamaletsos *et al*., 2007).

Coal layers, with a maximum thickness of 50 cm, are found in some locations just above the B3 horizon, covered by limestone of Upper Cretaceous age forming the thick layers of the Parnassus-Giona Unit (Kalaitzidis *et al*., 2010). Oxidation of pyrite inclusions in the coal resulted in the formation of acid fluids that percolated downwards to cause bleaching of the upper parts of the underlying bauxite (Kalaitzidis *et al*., 2010). This may have impacted on the distribution of REE within the bauxite, as under acidic conditions REE are easily weathered from aluminosilicates (Nesbitt, 1979; Fleet, 1984; Karadağ *et al*., 2009).

Bauxite production and red muds

The karst bauxite deposits of Greece are among the world's most important sources of bauxite for non-metallurgical products such as for chemicals and fused alumina. The main exploitable deposits are those in the Parnassus-Giona zone, with indicated reserves of 100 Mt (O'Driscoll, 2011). Bauxite production is predominantly from underground mining of the B3 horizon, with less from the deeper B2 horizons. The B1 horizon is currently not being exploited due to its greater depth. Alumina is refined at the Aluminium S.A. site using the Bayer process and the resulting waste red muds (700000 tpa (Anagnostou, 2010)) are dewatered

and stockpiled onshore. Deposition of dewatered red mud started in 2009; the approximate total volume accumulated to end 2015 is 5 Mt.

Bauxite REE geochemistry

Previous work on the Mortaş bauxite from Turkey (Karadağ *et al*., 2009; Hanilçi, 2013) and the Parnassus-Giona bauxites from Greece (Ochsenkühn-Petropoulou *et al*., 1991, 1994, 1995; Lymperopoulou, 1996; Valeton *et al*., 1987; Laskou, 1991, 2005; Laskou *et al*., 2010; Laskou and Economou-Eliopoulos, 2007, 2013), shows that they are enriched in the LREE relative to the HREE (Figure 6; Table 1). The Mortaş bauxites show a clear negative europium (Eu) anomaly on a chondrite-normalised plot (Figure 6), whilst the Greek bauxites only display a small negative Eu anomaly. These anomalies are likely to be inherited from the bauxite protoliths. The Greek bauxites show a positive Ce anomaly that is not present in the Mortaş bauxite. The Ce anomaly could be due to samples being collected from higher, near surface, relatively oxidising conditions where Ce is dominantly present as Ce^{4+}, rather than Ce^{3+}, and therefore fixed in oxides. Laskou and Andreou (2003) also identified a positive Ce anomaly in samples from the upper (B3) and middle (B2) bauxite horizons. Overall the Mortaş bauxite is more enriched in the REE (614 ppm *TREE* (Karadağ *et al*., 2009)) than the Greek bauxite (B3 horizon averages from 417 ppm (Valeton *et al*., 1987; [Economopolou-Kyriakopoulou, 1991]; Laskou, 1991, 2005; Ochsenkühn-Petropoulou *et al*., 1991; Laskou and Economou-Eliopoulos, 2007, 2013) to 527 ppm *TREE* (mixed bauxite from the B3 and B2 horizons sampled at the processing plant) (Ochsenkühn-Petropulu *et al*., 1994, 1995)); again this

464 could be due to sampling bias as the Greek samples were collected mostly from
465 higher horizons. Published data for karst-bauxite deposits from Italy (Boni *et al.,*
466 2013) and Turkey (Karadağ *et al*., 2009; Hanilçi, 2013) show similar trends in REE
467 content (Table 1), displaying relative enrichments in the LREE, particularly for Nd
468 and Ce.
469
470 **Results: rare earth element content of red muds**

471 All the sampled red muds show moderate enrichment in *TREE* (by up to 1.9 times,
472 Figure 6) when compared with the original bauxite (Figure 6; Table 1), with the
473 exception of 14/T/15. Small negative Eu anomalies in all red mud samples are likely
474 to have been inherited from the bauxite protolith. Small positive Gd anomalies are
475 also present in the red muds from both Greece and Turkey, but only occur in one
476 bauxite sample (Greece B3 horizon). The values for REE in the parent bauxites are
477 taken from the literature and will not necessarily correspond exactly to the specific
478 red mud sample being analysed.

479 Turkish red mud samples 14/T/16, 14/T/18 and 14/T/19 have an average content
480 of 1 090 ppm *TREE*, and are all relatively enriched in REE compared with the
481 published values for the parent bauxites (Figure 6; Table 1). Sample 14/T/15,
482 however, shows an overall depletion in REE relative to the Mortaş bauxite (*TREE*
483 150 ppm). This may be because this sample was taken from the far west end of the
484 pond (inset Figure 4), where the red mud cover is thin and therefore meteoric
485 waters may have leached out the REE, or alternatively, the sample may have come

from an unusually low REE bauxite feedstock. Turkish red mud samples 14/T/15-16 and 14/T/19 show a positive Ce anomaly, whilst sample 14/T/18 shows a negative Ce anomaly. This could be due to the oxidation state of Ce in the bauxite horizon from which the waste was derived. Sample 14/T/18 also has higher total HREE content, 356 ppm compared with an average of 208 ppm, which could also be explained if it was sourced from deeper within the bauxite. Within the bauxite profile, HREE complexes are more stable in the more alkaline conditions that occur at depth during bauxite formation (Johannesson *et al*., 1995, 1996; Mameli *et al*., 2007).

Greek red mud samples show similar REE patterns to the Turkish samples though they are generally less enriched in REE (Table 1; Figure 6). They also show a more homogeneous spatial distribution of REE, even though samples are from different mines within the B3 and occasionally the B2 layers. *TREE* values range between 800-900 ppm (up to 1000 ppm where Sc is included). All samples are characterised by Ce, La, Nd and Y enrichments. Distinct positive Ce and negative Eu anomalies are visible with minor enrichments in Tb and Gd also present. It should be noted that the samples have been individually analysed by slightly different methods and in different laboratories and as such are not directly comparable. However, these are representative samples from two large red mud storage facilities and so can be used to give an insight into European REE resources from alternative sources.

Resource potential

508 Whether red mud in Europe represents a potential resource for REE will largely
509 depend on whether proven bench- and pilot-scale processing and beneficiation
510 techniques for this material can be up-scaled for production. For a detailed
511 overview of these, readers are directed to Binnemans *et al*., 2015. In addition, a
512 clear understanding of the volume of red muds present in Europe will aid in
513 assessing whether these resources are viable. The remaining discussion will focus
514 on this second aspect.

515 Table 2 utilises the data from Figure 3 and Table 1 to estimate *TREE* to calculate
516 average total contained REE, Nd and HREE in the red muds of Europe. Taking an
517 average value of 1000 ppm REE in red mud gives a range of resource potentials in
518 Europe. If the REE were to be extracted at an efficiency of 50% (Ochsenkühn-
519 Petropoulou *et al.,* 1996), then the minimum quantity of available REE would be 100
520 000 t, while at a maximum there are approximately 270 000 t REE in European red
521 muds. 425 Mt of red mud (see average cumulative figure in Table 2) at 1000 ppm
522 REE would contain 430 000 t of REE, which at 50% recovery could produce 210 000 t
523 REE. These figures are based on stored red mud stocks produced from alumina
524 refining in Europe since 1972, and as such, are a conservative estimate for the
525 potential resources available from red muds in Europe.

526 In a global context, around 150 Mt of red muds are currently being produced per
527 year with up to 150 000 t of contained REE going to waste ponds. This equates to
528 approximately 172 500 t REO, using 1.15 as an average element-to-stoichiometric
529 oxide conversion factor. Annual global production of REE, expressed as tonnes of
530 REO, was approximately 100 170 t in 2013 (BGS, 2015). It is thus clear that there is
531 potential for red muds to make a substantial contribution to the global supply of
532 REE.

Taking neodymium as an example, the potential Nd resources in red muds across Europe is approximately 20000 - 45000 t. This equates to greater than four years of global production, calculated at approximately 23000 t per year (2011 data) (EC, 2013 and references therein). The figures from Europe as a whole indicate that HREE (Eu to Lu +Y) resources in red muds could be as much as 60000 t. With the development of selective beneficiation techniques it may be possible to prevent the oversupply of LREE as is the current market situation (in 2015), and preferentially produce the more in-demand elements such as neodymium and dysprosium. An important caveat is that these figures represent red mud waste from all bauxite types processed in European refineries. Annual importation of bauxite into Europe equalled more than 13.5 Mt in 2013, (the last year for which figures are available) (BGS, 2015), with major import partners including Guinea and Brazil (data from UN Comtrade Database, accessed May 2015). Major bauxite deposits in these countries are from lateritic-type bauxites rather than karst-type bauxites. Taking this into consideration, further work on characterising the REE content in lateritic bauxites in Europe and in the known red mud storage facilities across Europe would further refine any initial resource estimates.

5 Mt of red muds are currently 'dry' stacked at Aluminium S.A. in Greece while at least 10 Mt of red muds are contained in the Seydişehir tailing ponds in Turkey, with waste material being produced throughout the year. New data for REE in red muds from stored waste facilities in Turkey and Greece demonstrate their potential as REE resource. Total REE in red muds from the two sites is approximately 12000 t, assuming an average of 1000 ppm REE in the red mud and an 80 % recovery (Borra *et al*., 2015).

Discussion

558 It is clear that red muds represent a significant potential resource of REE in Europe.
559 Understanding the REE content of red muds is essential for robust resource
560 estimation. Several factors may control the content and distribution of REE within
561 red muds. These include: 1) the REE content and mineralogy of the bauxite
562 precursor; and 2) the mineralogy of the REE within red mud ponds. The
563 development of industrial-scale processes to extract REE from red mud is
564 fundamental in establishing the economic viability of these potential resources.
565
566 *REE in bauxite and red mud*
567 The nature of, and mechanisms causing, variations in REE distribution in bauxites
568 are highly complicated with no one model fitting all deposits. In particular, the
569 effects of fractionation between the LREE and HREE, REE scavenging by Fe-rich
570 mineral phases, and changes in redox are not well understood. Although bauxites
571 are highly variable in their REE contents (e.g. from approximately 100 ppm to
572 greater than 2 300 ppm in bauxite from Parnassus-Giona (Laskou and Andreou,
573 2003)), in general there is often, but not always, an overall passive enrichment
574 downwards towards the limestone footwall. The importance of this is that REE
575 concentrations in red muds will be directly proportional to depth in the original
576 bauxite. If the original bauxite does not contain sufficient levels of REE, then REE
577 extraction from the red mud is unlikely to be viable, even with the recognised
578 enrichment factor of REE, including Sc and Y, from bauxite to red muds of
579 approximately 1:2 (Ochsenkühn-Petropoulou *et al*., 1994; Wagh and Pinnock,
580 1987). Selection of red muds from processing of a particular bauxite horizon, or a
581 mixture of particular horizons, could potentially be carried out to produce ideal
582 blends for REE production.
583 The distribution and nature of the REE-bearing phases and minerals in red mud is

584 poorly defined. The association of REE with iron and manganese phases is widely
585 acknowledged in the literature, as is the presence of authigenic and detrital REE-
586 bearing minerals. However, much more work is necessary in order to fully
587 understand the distribution and mineralogy of REE in red muds. This will, in turn,
588 allow a clear economic quantification of the potential REE resources in European
589 red mud.
590
591 *REE processing*
592 Processing techniques for the two most common REE-containing minerals,
593 bastnäsite and monazite, are quite well understood and have well established
594 beneficiation flow sheets. Processing streams are being developed for other REE-
595 bearing minerals such as eudialyte (www.eurare.eu), however, these do not make
596 a significant contribution to current REE production (Jordens *et al*., 2013). This
597 situation is likely to change with growing commercial demand for REE, with
598 increased opportunities to develop new rare earth element deposits with a wider
599 range and less well-understood mineralogy.
600 Successful extraction of REE from red muds has been achieved at both bench and
601 pilot scales (Wagh and Pinnock, 1987; Ochsenkühn-Petropoulou *et al.,* 1996, 2002;
602 Smirnov and Molchanova, 1997; Tsakanika *et al*., 2004; Qu and Lian, 2013; RUSAL,
603 2014; Borra *et al*., 2015). However, further development of these techniques is
604 necessary in order to make these resources economically viable. In order for REE to
605 be extracted most economically, ideally an additional processing stream for REE
606 would be developed as an add-on to the Bayer process itself.
607 Taking an average concentration of 1000 ppm REE for red muds, REE by-product
608 production from current, karst-bauxite sourced, alumina production,
609 approximately 1.5 Mt annually (BGS, 2015), could equate to up to 1500 t REE per

610 year. By-product production of REE from European bauxite exploitation of
611 appropriate deposits could result in a steady, secure supply of REE within Europe.
612 In order to benefit from the red muds that are currently stored onshore, it would
613 be advantageous to regard the re-mining of the tailing ponds as a viable additional
614 resource. It has been shown that it is not only the REE that are potential by-products
615 of the red muds, research is also on-going into the extraction of Ga and Sc
616 concentrates from red mud waste at Orbital Aluminae, Canada and Rusal, Russia,
617 respectively. Additionally, base metals and other critical raw materials are
618 frequently found in the waste material, depending on the original composition of
619 the source, and are potential by-products of further extractive processing.
620 One positive aspect of the onshore stockpiles of red muds in Europe is that these
621 are generally found in politically stable jurisdictions with an obvious history of
622 mining and therefore, possibly without strong local anti-mining sentiment.
623 Additionally, working on stockpiled waste is a more environmentally friendly option
624 as no additional mining, and minimal, if any, grinding, is required. It also could
625 provide an independent source of REE and protect REE-resource poor countries
626 from export quotas and price fluctuations (Binnemans and Jones, 2015).
627 The current lack of plant-scale methods of extracting REE from the red muds is a
628 potential obstacle to the development of these resources. Ongoing research, such
629 as that carried out by the FP7 funded EURARE and Mud2Metals projects, is tackling
630 these challenges. Under the recent patent granted to Orbite Aluminae Inc. (Patent
631 No. 14/371,364, Orbite, 2015) for the 'Orbite Process', a red mud processing plant
632 at Cap-Chat, Québec, Canada, is expected to begin production in the last quarter of
633 2015 and aims to produce a REE concentrate as one of the products. It also aims to
634 reprocess the red muds for alumina, as inefficiencies in the Bayer Process can result
635 in losses of up to 25% of the aluminium to the waste. The success of this

636 beneficiation stream could have a significant impact on the production of REE from
637 red mud waste. However, it has been shown that the extraction of REE from red
638 muds would do little to reduce the volume of red muds produced and so the
639 development of alternative uses for red muds is still a key societal and
640 environmental challenge (Klauber *et al*., 2011).
641 There is a lack of collated data on red mud production and storage globally,
642 although it has been recognised internationally that the disposal, treatment and
643 maintenance of red mud ponds is of key social and environmental importance. This
644 issue was highlighted in 2010 with the tragic failure of the red mud pond at
645 Kolantár, Hungary. This has been addressed partly by the development of the
646 Bauxite, Residue and Disposal Database (BRaDD) (Gräfe *et al*, 2011). Maintaining
647 and updating such a large database needs the support of industry but can aid in
648 developing an appropriate strategy for the management of red mud (Power *et al*.,
649 2011), including the possible extraction of valuable metallic commodities.

650 **Conclusions**

651 Potential resources of REE are present in significant quantities in red mud storage
652 facilities globally. Of these red muds, those that are derived from karst-type
653 bauxites are thought to be the most prospective for REE given the alkaline
654 conditions under which they form, where the pH due to the underlying limestone
655 retards mobility of the REE and traps the REE in the bauxite ore. In Europe, karst-
656 type bauxites are most common in the Mesozoic limestone of the Mediterranean.
657 Historic and current exploitation of these bauxite deposits has resulted in REE-
658 enriched red muds stored onshore across the region. This study has identified
659 combined potential resources of up to a maximum of 15000 tonnes REE contained
660 in red muds in two areas, one in Greece, the second in Turkey. A full exploration

campaign would be needed to investigate and evaluate the red mud waste tips. The original heterogeneity of the bauxite could lead to heterogeneous waste tips that would need careful resource estimation. Development of efficient beneficiation and processing techniques and further work on understanding the distribution of REE in red muds, in conjunction with the quantification of resources in European red mud stocks, could lead to the development of sustainable REE production and utilisation of waste material in Europe.

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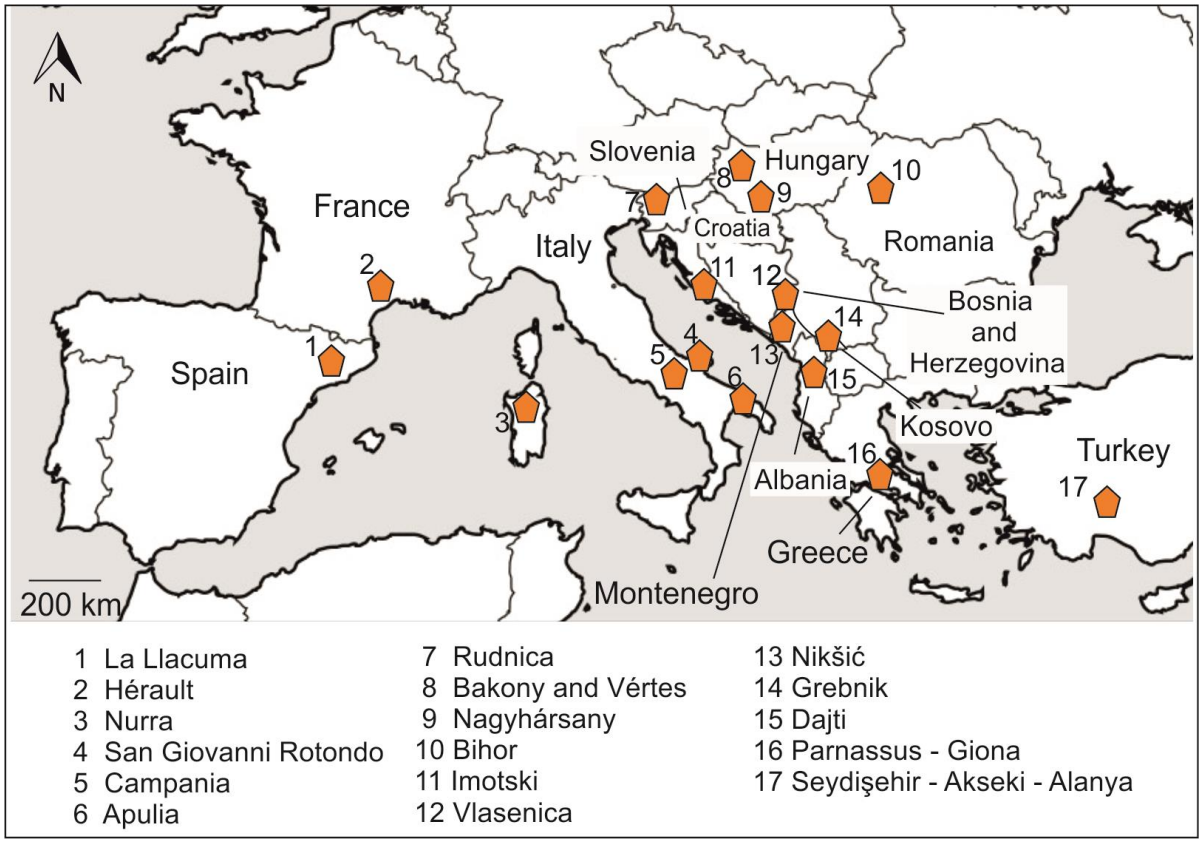
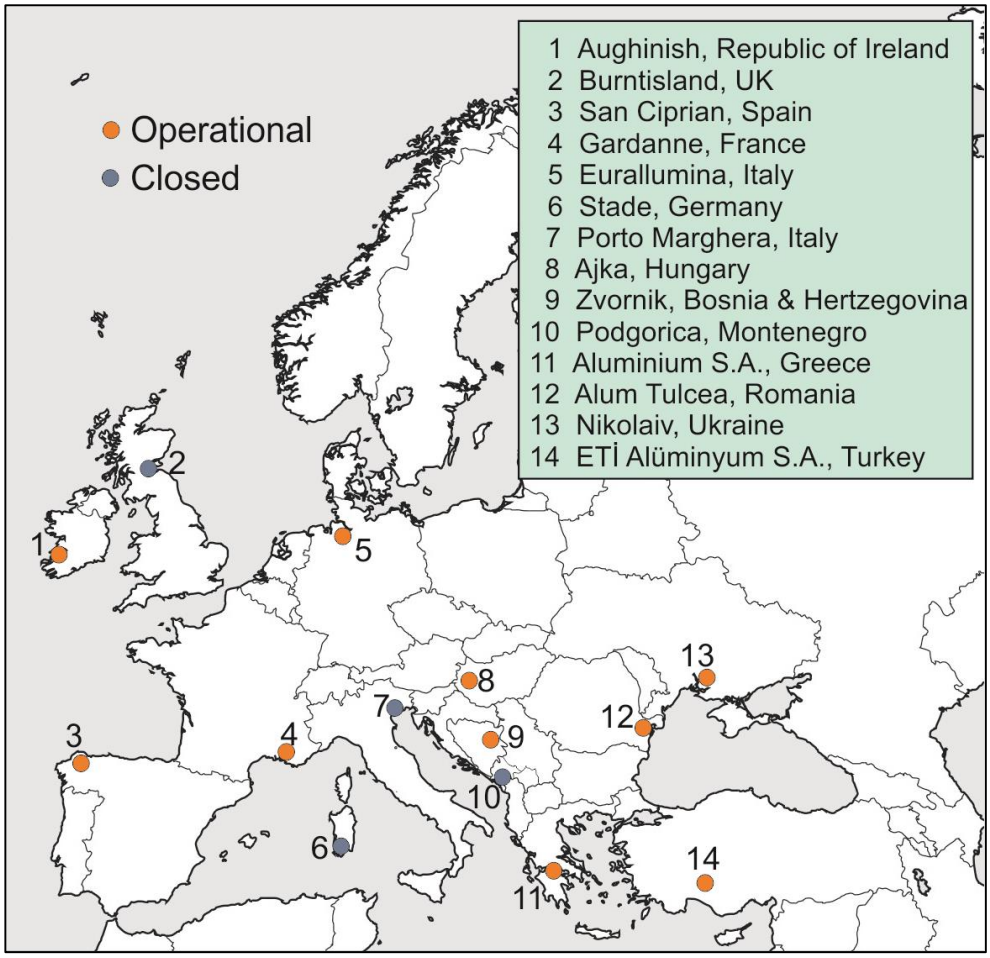


682

683 Figure 1: European karst-bauxite deposits and mines in the circum-Mediterranean

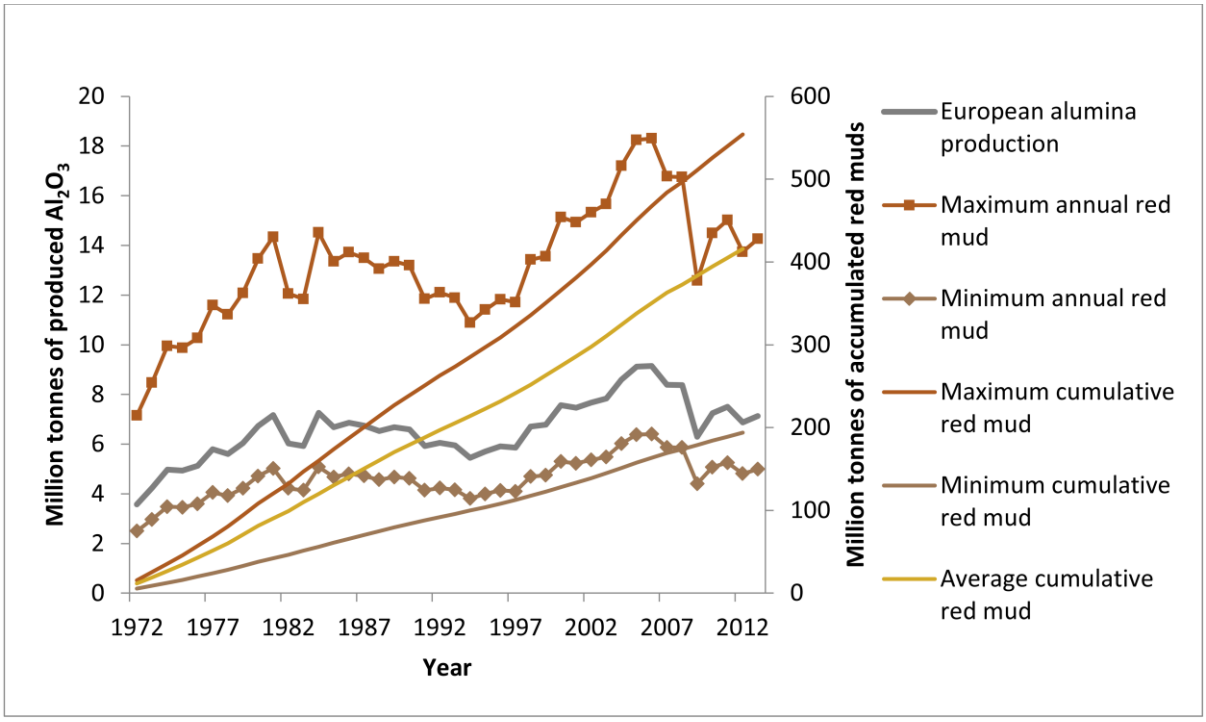
684 region (after Patterson, 1967).

685 

686 Figure 2: Alumina refineries that utilise the Bayer process, both in use and

687 abandoned in Europe (adapted after Power *et al*., 2011).

688



689

690 Figure 3: Time series data of European alumina production since 1972 (data from
691 British Geological Survey World Mineral Statistics database). Greek data are
692 excluded before 2009 due to the disposal of red muds at sea. Annual European
693 alumina production is on the left-hand vertical axis, and cumulative average,
694 minimum and maximum volumes of red muds stored in European onshore tailing
695 ponds or 'dry' stacks are on the right-hand vertical axis.

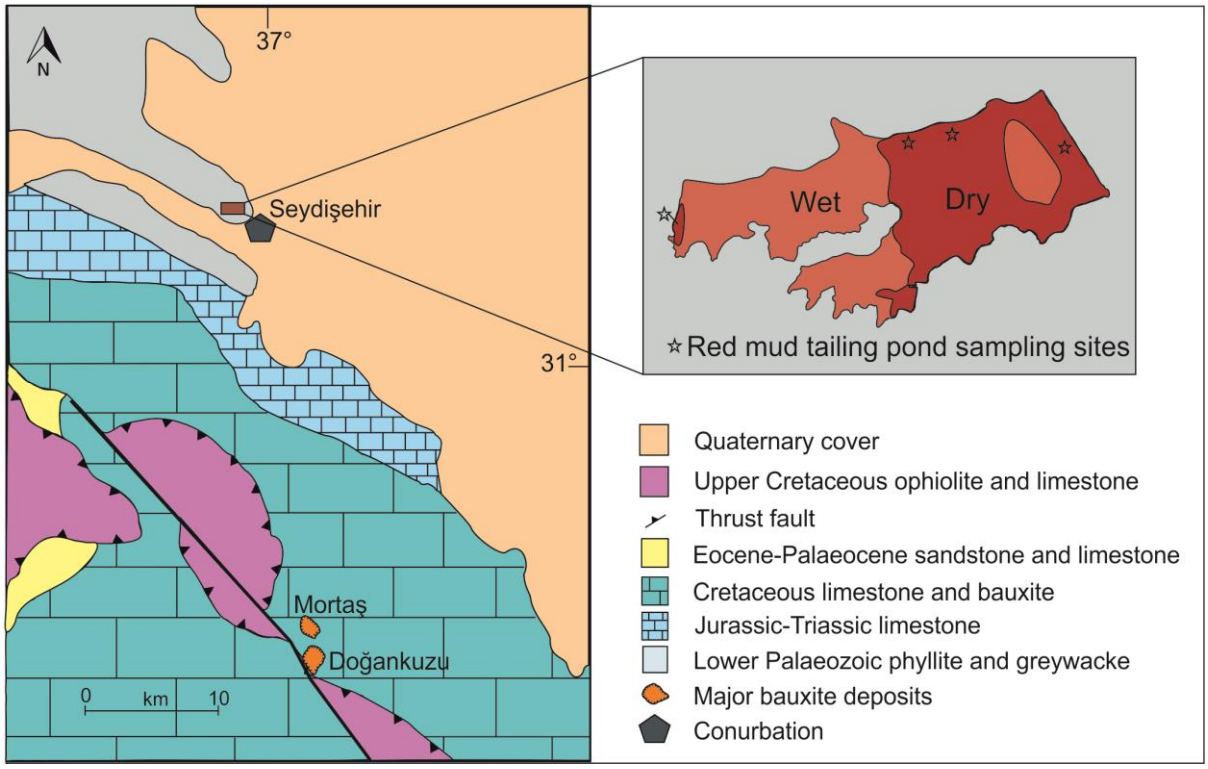


Figure 4: Geology of the Seydişehir area, Turkey (adapted with permission from Öztürk *et al*., 2002 and *pers comm.*) showing key geological features, the location of the red mud tailing pond and sampling sites.

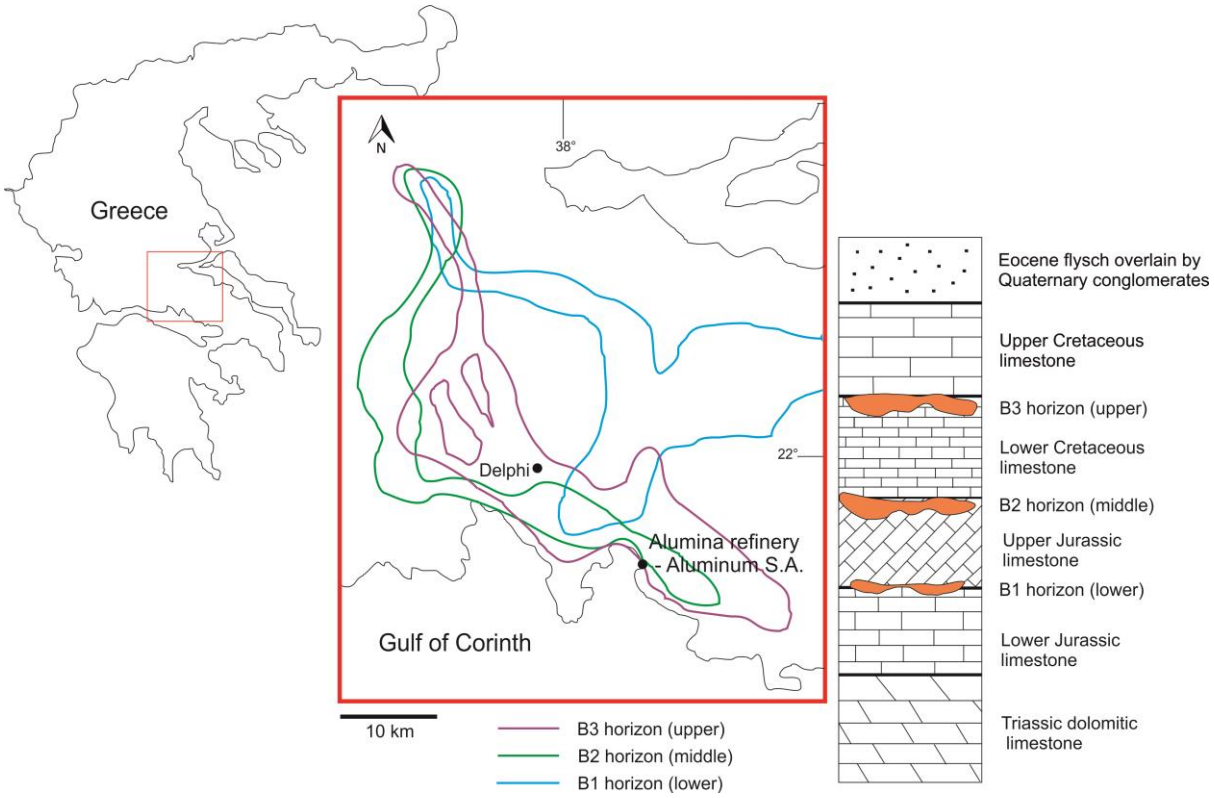


Figure 5: Regional distribution and simplified stratigraphic column of the three bauxite horizons (Petrascheck and Mack, 1978; Valeton *et al*., 1987; schematic stratigraphic column reproduced with permission after Laskou and Economou-Eliopoulos, 2013).

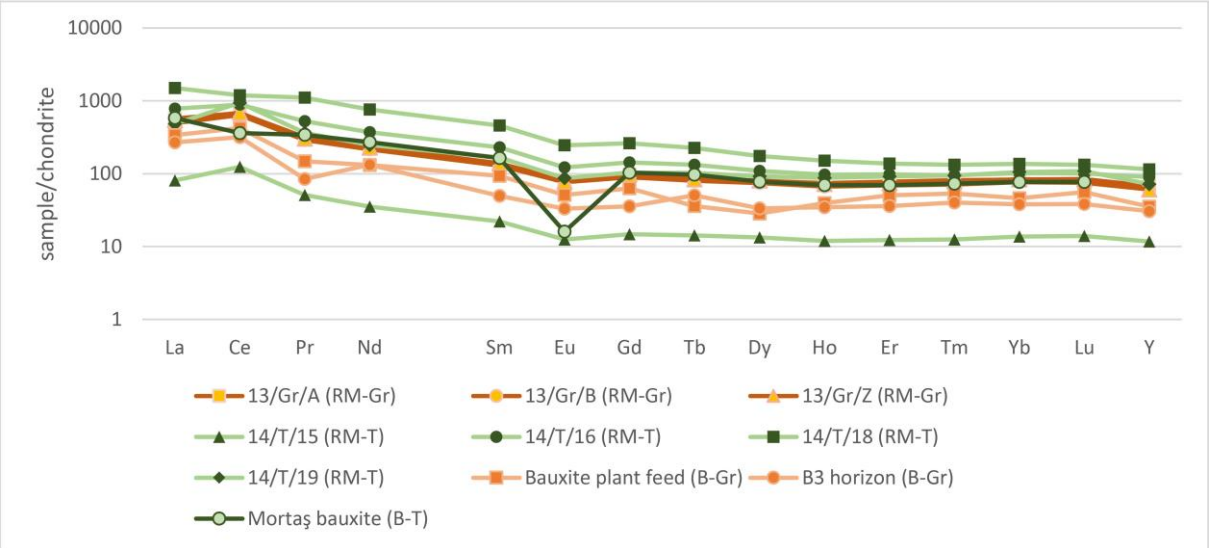


Figure 6: Chondrite-normalised (MacDonough and Sun, 1995) REE patterns for red mud samples from Greece and Turkey compared with published values for the Greek plant feed bauxite and the B3 horizon (Ochsenkühn-Petropoulou *et al*., 1994, 1995) and the Mortaş bauxite (Karadağ *et al*., 2009). Red muds: RM; bauxites: B; Turkey: T; Greece: Gr.

	Red muds, this study							Bauxite, literature data					
Sample name	13/Gr/A	13/Gr/B	13/Gr/Z	14/T/15	14/T/16	14/T/18	14/T/19	Mortaş bauxite, Turkey*	Bolkardağı BP bauxite, Turkey*	Bolkardağı OS bauxite, Turkey*	Plant feed bauxite, (B3+B2) Greece*	Parnassus -Giona B3 bauxite, Greece*	Regia Piana bauxite, Italy (GBRX 8)*
	Parnassus-Giona red mud, Greece (this study)			Seydişehir red mud, Turkey (this study)									
La	134.9	117.2	129.3	19.2	185.9	356.2	114.8	137.6	107.6	35.8	80.2	64	87.7
Ce	416.9	391.3	421	76.1	543.2	728.5	576	221	233.5	159	259.5	195	154.1
Pr	29.6	27	28.3	4.7	49	102.7	33.9	31.7	24.7	7.1	13.8	7.8	19.7
Nd	107.4	99	104	16.2	169	346.7	113.5	124.7	88.1	26	59.8	60.3	74.2
Sm	20.5	19.1	20.5	3.3	34.1	67.9	24.7	24.2	17.2	5.2	13.8	7.3	13.4
Eu	4.5	4.3	4.4	0.7	6.9	13.8	4.9	0.9	3.8	1.2	2.8	1.8	2.8
Gd	19.3	17.8	19.6	0.5	4.8	8.2	3.7	20.6	17.9	6.4	12.5	7.1	12
Tb	3.1	2.8	3	2.9	28.5	52	20.6	3.5	3.2	1.4	1.3	1.8	2.1
Dy	19.7	18.2	19.9	3.3	27	42.9	22.7	19.1	19.6	9.6	7	8.2	11.9
Ho	4.1	3.6	3.9	0.7	5.3	8.2	4.8	3.8	4.2	2.3	2.1	1.9	2.5
Er	12.4	11	11.8	2	15.7	21.9	14.8	11.2	12.5	7.6	8	5.7	7.7
Tm	2	1.7	1.9	0.3	2.4	3.3	2.3	1.8	2	1.3	1.3	1	1.2
Yb	13.3	12.2	13.5	2.2	16.4	21.9	17	12.4	12.2	8.6	7.4	6.1	8.3
Lu	2.1	1.8	2.1	0.3	2.5	3.3	2.7	1.9	1.9	1.3	1.3	0.9	1.2
Total Lanthanoids	790	727.5	783.2	132.5	1090.6	1777.4	956.2	614.4	649.3	674.6	471.3	369.4	497.6
Y	106.2	95.4	95.2	18.4	141.3	180.2	112.7	N/A	78.2	126.2	55.4	48	56.7
TREE	896.2	822.8	878.4	150.9	1231.9	1957.5	1068.9	614.4	727.5	800.8	526.7	417.4	554.3

711

712 Table 1: REE (ppm) contents in red mud samples from Turkey and Greece,
713 (*literature data). Averaged values are for bauxite feed (a blend of horizons B3
714 and B2) from the Aluminium S.A. alumina refinery, Greece (Ochsenkühn-
715 Petropulu *et al*., 1994, 1995); horizon three (B3) of the Parnassus-Giona bauxite
716 province, Greece (Valeton *et al*., 1987; [Economopolou-Kyriakopoulou, 1991];
717 Laskou, 1991, 2005; Ochsenkühn-Petropoulou *et al*., 1991; Laskou and Economou-
718 Eliopoulos, 2007, 2013); the Mortaş bauxite, Turkey (Karadağ *et al*., 2009) and, for
719 comparison, the Baharpınarı (BP) and Öşün (OS) bauxite deposits in the Bolkardağı
720 bauxite province in Turkey (Hanilçi, 2013) and the Regia Piana bauxite (GBRX 8),
721 Italy (Boni *et al.,* 2013).

	Red mud (Mt)	TREE concentration (ppm)[e]	TREE content (Mt) (@ 50% recovery)	Nd concentration (ppm)[e]	Nd content (Mt) (@ 50% recovery)	HREE concentration (ppm)[e]	HREE content (Mt) (@ 50% recovery)
Minimum cumulative	200	1000	0.10	150	0.02	200	0.02

Maximum cumulative	550	1000	0.27	150	0.04	200	0.06
Average cumulative	425	1000	0.21	150	0.03	200	0.04

722

723 Table 2: Cumulative minimum, maximum and average tonnages of red muds
724 stored onshore in Europe since 1972 and their estimated contents of *TREE*; Nd;
725 and $HREE_{(Eu\text{-}Lu+Y)}$; (^{e} estimate).

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