

# A Geological Study of the Potential for Rare Earth Element By-Product Recovery from Greek Bauxite Deposits

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**MSc by Research Thesis** 



# A Geological Study of the Potential for Rare Earth Element By-Product Recovery from Greek Bauxite Deposits

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Evangelos Mouchos, September 2015

#### Abstract

Rare earth elements (REE) are now classed as 'critical' because of rising global demand as a result of their use in many new, green and emerging technologies. However, there is currently restricted supply, dominated by China (>90 per cent), and extremely low rates of recycling (less than 1 per cent). These factors increase the urgency to identify alternative REE resources. Bauxite, apart from being the main commercial source of aluminum, also has the potential to become an important resource for REE and other critical metals.

The Parnassus-Giona bauxite deposits (B1-B3 from oldest to youngest) in Greece were formed by lateritic weathering processes. The eroded material, derived from parent aluminosilicate rocks and ophiolites, accumulated in the karst topography of Upper Jurassic to Middle Cretaceous limestone to form large bauxite deposits. The crystallisation of authigenic REE-bearing minerals towards the base of the bauxite occurred due to the downward transport of relatively mobile elements (including the REE). *Per descensum* enrichment results occasionally in very high REE concentrations.

Aluminium S.A. is processing over 1.5 Mt of bauxite annually using the Bayer Process and as a result is producing approximately 700,000 t of red mud waste. Red muds from Greek B3 and B2 bauxite deposits contain an average of about 900 ppm  $\Sigma$ REE. The B3 bauxite deposits from which they are mostly derived usually contain lower  $\Sigma$ REE (approximately from 150 to 700 ppm), varying with location and depth. The red muds therefore contain approximately twice the levels of REE than the original bauxite, making them a potential alternative REE resource. However, compared to carbonatite REE deposits such as Mountain Pass that contains 8.24% REO on average and 5% REO cut-off grade, Greek bauxites and red muds commonly have less than 0.1% of average REO and cut-off grade. Moreover, Greek bauxites and red muds are also lagging in REE proportions compared to other similar REE resources such as the Jamaican red muds (0.23-0.38 wt.%  $\Sigma$ REE+Y) or the Chinese HREE enriched ion adsorption deposits (0.03-0.35% REO).

This study compares REE concentrations in bauxite and corresponding red mud waste from bauxite deposits in Greece to assess the feasibility of efficient REE extraction either by selective mining of REE-enriched bauxites or red mud waste stockpiles. In more detail, bauxite samples were collected from

recently operating B3 underground bauxite mines and red mud waste samples from dehydrated stockpiles. These were examined for their major, minor (XRF) and trace elements (ICP-MS), main minerals (optical microscopy and XRD) and most importantly REE-bearing minerals (SEM and EPMA). Finally, various weathered REE-rich samples (bauxites, laterites and kaolinites) and their byproducts (e.g. red muds) were analysed in order to determine if they contain any easily leachable phases.

The main outcome of the study is that both bauxites and red muds can be considered as REE potential resources, containing REE that their cut-off grade will not exceed the mining and processing costs, and in a form that is relatively easily recoverable using standard or modified leaching protocols. More precisely, bauxite could have a cut-off grade of 0.1% or more only at specific HREE enriched locations near the bedrock of the deposits. On the other hand, red mud as a waste of blended bauxite originating from various mines could contain 0.1% REO on average including LREE, HREE, Sc and Y. In the same context, red mud waste could be economically exploitable at a lower cut-off grade in comparison with a stand-alone bauxite mine because of the significantly lower mining costs. However, further work is required to determine the most economically and environmentally feasible method to extract REE from bauxites, before the Bayer process, or after it from red muds.

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# List of Abbreviations

ANRT	Association Nationale de la Recherche Technique		
AUTh	Aristotle University of Thessaloniki		
B1, B2 and B3	1 <sup>st</sup> , 2 <sup>nd</sup> And 3 <sup>rd</sup> Bauxite Horizon		
BCR	European Community Bureau of Reference		
BGS	British Geological Survey		
BSE Image	Back-Scatter Electron Image		
CSM	Camborne School of Mines		
EDS	Energy Dispersive Spectrometer		
EPMA	Electron Probe Microanalyser		
EU	European Union		
HFSE	High Field Strength Elements		
HREE	Heavy Rare Earth Elements		
IAI	International Aluminium Institute		
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry		
IGME	Institute of Geology and Mineral Exploration of Greece		
IMO	Internationtal Marine Organisation		
IX	Ion Exchange		
LILE	Large Ion Lithophile Elements		
LLE	Liquid-Liquid Extraction		
LOI	Loss On Ignition		
LREE	Light Rare Earth Elements		
NHM	National History Museum of London		
REE	Rare Earth Elements		
REO	Rare Earth Oxides		
RM	Red Mud Waste		
SEM	Scanning Electron Microscope		
USGS	US Geological Survey		
XRD	X-Ray Diffraction		
XRF	X-Ray Fluorescence		

### 1. Introduction

#### 1.1 Greek Bauxite and its By-Products as an Alternative REE Resource

Mining has been part of Greek civilization since prehistoric times, when Greeks began extracting non-metallic minerals and metals for use. In the last 70 years significant mining operations in Greece have focused on nickel, aluminum, chromium and iron-manganese deposits, as well as lead-zinc-( $\pm$ Cu,  $\pm$ Au,  $\pm$ Ag) sulfide occurrences. According to Tsirambides and Filippidis (2012) the total value of the indicated metallic mineral reserves of Greece exceeds £52 billion. It should also be mentioned that Greece is the only country in the EU with large deposits of manganese, chromite, aluminum and nickel and is the leading producer of aluminum (from bauxite) and nickel (from laterite) in the EU (Melfos and Voudouris, 2012).

Bauxite and red mud, the waste product of the Bayer process that produces alumina from bauxite, contain significant amounts of rare earth elements (REE) (e.g. Ochsenkühn-Petropoulou et al., 1991; Laskou and Andreou, 2003). The 2010-11 REE crisis followed by the launch of the EURARE project indicated a realistic REE exploitation potential for the secondary REE resources of Greece and Europe.

#### **1.2 Aims of this Project**

Among the main research goals of this thesis were the study of the spatial distribution and *per descensum* enrichment of REE towards understanding REE geochemical behavior and the identification of authigenic REE minerals in order to understand under which conditions those minerals were formed. As far as the red mud waste is concerned, the focus was on the comparison and correlation of critical and REE concentrations with those in the initial bauxite. For this purpose, samples were obtained from the Delphi-Distomon S.A. (subsidiary of Aluminium S.A.) underground bauxite mines and Aluminium S.A. red mud waste stockpiles.

Furthermore, the potential to develop a sequential REE leaching protocol for various weathered REE rich rocks and their by-products was investigated. Therefore, as well as Greek samples, Jamaican bauxite and red mud waste and Mt. Weld (Australia) laterites were analysed. The aims of this project in a nutshell were:

- To investigate the mobidity of REE in bauxite profiles in order to identify if all REE show the same behaviour and precipitate downwards; and which factors affect the downward REE enrichment.
- 2. To identify which REE minerals (detrital or authigenic) occur in bauxite, where these are getting concentrated and how the authigenic REE minerals were formed.
- 3. To develop or adapt a realistic model that describes the behaviour of REE and the formation of authigenic REE minerals in bauxite.
- 4. To estimate the average REE concentrations in bauxite and red mud waste and evaluate the total REE contents that are hosted the Greek bauxite deposis and red mud waste stockpiles, in order to determine if a potential exploitation of REE is feasible.
- To test if bauxite and red mud waste contain easily leachable REE phases, develop a REE leaching protocol and investigate the most suitable part of the bauxite mining-alumina production chain for efficient REE leaching.

# 2. Bauxite Formation and Characteristics

#### 2.1 Introduction

This chapter summarises briefly the mineralogy and chemistry of bauxite and presents its types. Furthermore, it presents the formation mechanism of bauxite in general and focuses on the formation of authigenic REE bearing minerals particularly in karst bauxite.

#### 2.2 Bauxite Ore Chemistry

Bauxite is a rock type that consists of several minerals, mainly aluminum hydroxides, such as boehmite, diaspore and gibbsite, and is the main raw material for aluminum production. Initially, the term bauxite was used by Berthier, in 1821, which was the first to analyse aluminium-rich rocks from Les Beaux-de-Provence area in France. Later on, Dufrénoy in 1845 characterized these aluminum oxide-rich sediments. Lieblich in 1892 also used the term bauxite for the gibbsite-rich laterites of Vogelsberg (Germany). Nowadays, bauxite is used to describe aluminum-rich and alkali-, alkaline earths- and silica-poor weathering and erosion products.

Bauxite may be monohydrate if it consists predominantly of boehmite [( $\gamma$ -AIO(OH)] or diaspore [( $\alpha$ -AIO(OH)] or trihydrate if it consists mainly of gibbsite (AI(OH)<sub>3</sub>).It can be found as a mixture of monohydrate and trihydrate bauxite. The composition of bauxite in terms of major oxides is approximately as follows:

- Al<sub>2</sub>O<sub>3</sub> (40-90%)
- Fe<sub>2</sub>O<sub>3</sub> (0-25%)
- SiO<sub>2</sub> (2-30%)
- TiO<sub>2</sub> (2-5%)
- CaO (0-3%)

Bauxite also contains many trace elements including Ce, Co, Cr, Cu, Ga, Ge, In, La, Mn, Nb, Ni, Pb, Sr, U, V, Y, Zn and Zr.

The largest Greek bauxite deposits occur in the Parnassus-Giona zone (Fig. 2.2) and belong to the "karst" type. They are derived from the lateritic

weathering of basic rocks (such as basalt, diabase and gabbro) of ophiolitic complexes that abound in the Subpelagonian zone (Valeton et al., 1987). The color of Greek bauxites depends mainly on its composition and especially on the presence of iron oxides or hydroxides. Bauxites can be distinguished as:

- 1. Red or reddish-brown (presence of hematite)
- 2. Yellow (presence of goethite)
- 3. Gray (with small amounts of iron oxides)
- 4. White (absence of iron oxides)

In order to be economically exploitable, bauxite must contain over 45%  $AI_2O_3$ , less than 20%  $Fe_2O_3$  and up to 5%  $SiO_2$ . In Greek bauxites the  $AI_2O_3$  content usually ranges between 49%-65% while the content of the remaining major oxides is about 18%-24%  $Fe_2O_3$ , 0-5% CaO, 2%-10%  $SiO_2$  and 0.5-3%  $TiO_2$ . Additionally, the Cr and Ni content can reach 2,000 ppm.

#### 2.3 Bauxite Types and Classification

Lateritic weathering of aluminosilicate rocks is the main mechanism of bauxite deposits formation. The products of weathering can either remain in situ to form autochthonous deposits, or may be transferred to another place to form allochthonous deposits.

In terms of age, bauxites generally cover a wide range, as they can be found from Precambrian right through to Holocene formations. Lateritization processes for the formation of Fe-Ni laterite deposits and consequently the formation of allochthonous karst bauxite deposits occurring in central Greece started during Jurassic and ended at the Cretaceous (Fig.2.1).

Owing to the huge variety of bauxite types and their individual characteristics (such as geological, morphological, mineralogical, paleontological, etc.), various classification methods have been proposed. The most common and widely approved classification, which was also used by Valeton (1972), Bushinsky (1975) and Bárdossy (1982), divides bauxite deposits into three main types:



Figure 2.1. Middle Jurassic continent reconstruction (about 170 Ma) (upper) and Middle Cretaceous continent reconstruction (about 100 Ma) (lower). 1) Bauxite deposits, 2) Hercynian orogenic belts and 3) Mesozoic and Tertiary orogenic belts (Smith et al., 1973; Bárdossy, 1982). The red points show the position of Greek bauxite deposits.

A) Lateritic-type (88% of bauxite reserves worldwide): These deposits are very extensive spatially, occur as layers and are formed by lateritic *in situ* weathering of aluminosilicate-rich rocks, which are usually their bedrocks. Lateritic-type deposits that were formed by weathering of alkaline rocks occur in Brazil (Mines Gerais), Guinea (Isles des Los) and the USA (Arkansas). Lateritic-type deposits formed from "acidic rocks" can be found in Africa, Australia, Brazil, India and Indonesia. Finally, deposits of lateritic bauxite that were formed due to the weathering of "basic rocks" are located in India (Gujerat and Madya Pradesh), Guinea, N. Ireland and the USA.

*B) Tikhvin type (0.4% of bauxite reserves worldwide):* The bedrock of such deposits consists of aluminosilicate rocks, the surface of which is eroded. The bauxite material is transferred from another area and has no relation to the underlying rocks. This type occurs only in five bauxite locations (all in the former Soviet Union) and has taken its name from the Tikhvin district (SE of St. Petersburg, Russia).

*C)* Karst type (11.6% of bauxite reserves worldwide): Karst bauxites are formed by the erosion of lateritic bauxites. The weathered material is transported and deposited (as clastic sediments) in mechanical traps of karstic limestones. In this type of deposits, bauxite lies on anomalous karstified surfaces of limestones and dolomitic rocks. Karst bauxites are characterized by an unconformity between the bedrocks and bauxite layers. Greek bauxite deposits belong to the karst type; hence a more detailed analysis will follow in the next chapters. The vast majority (92%) of karst bauxites in the world are located in orogenic arcs, whereas only 8% is intracontinental. On the contrary, 96.5% of lateritic bauxite type and 100% of Tikhvin type occur in intracontinental areas.

Karst bauxites include six types of deposits (Bárdossy, 1982; Bárdossy, 1989):

1) Mediterranean type (76% of global karst bauxite): This is the most common type, including bauxite deposits occurring in most Mediterranean countries (such as Italy, France, Spain, Bosnia and Herzegovina, Montenegro, Kosovo and Greece), Hungary and Russia. Furthermore, small deposits of this type are

located in Switzerland, Austria, Czech Republic, Slovakia and Bulgaria (Fig. 2.2).



Mediterranean region (modified after Patterson, 1967).

2) Timan type (14% of global karst bauxite): This type is used to describe bauxite deposits that are located in Timan mountains, Russia (Diomina, 1977). Bauxite fills large and shallow karst depressions, with their upper part consisting of bauxite and the lower part of continental sediments.

3) Kazakhstan type (7% of global karst bauxite): In this type deep karst depressions are filled with various continental sediments. Bauxite occurs as intercalated bodies at several levels.

4) Ariège type (2% of global karst bauxite): This type includes the bauxite deposits of Ariège area of the Pyrenees Mountains, France (Combes, 1969) and deposits of Lika area in Croatia (Sincovec, 1970). Ariège type is used to describe a peculiar transition between karst and lateritic deposits.

5) Salento type (1% of global karst bauxite): This type includes bauxite deposits of Salento peninsula in Italy as well as deposits in Hungary and Turkey

(Cottechia and Dell'Anna, 1959). Salento type is used to describe redeposited bauxite pebbles, imbedded in red clays.

6) Tula type (less than 0.1% of global karst bauxite): This type is used to describe accumulations of gibbsite precipitating in karst depressions as a product of pyrite oxidation.

Finally, instead of lateritic and karst bauxites, some authors use the terms siliceous and calcareous bauxite. Bárdossy (1964) suggested the classification of bauxites shown in Fig. 2.3, which is based on:

- 1. Iron oxides and hydroxides content
- 2. Clastic material content
- 3. Halite minerals content, and
- 4. Clay minerals content



Figure 2.3. Petrographic classification of bauxites and their relation to the argillaceous rocks and sedimentary iron ores according to Bárdossy (1964). 1) Most frequent rock facies in nature and 2) frequent rock facies.

Whereas, Valeton (1972) proposed a petrological classification of bauxites related to clay rocks (Fig 2.4):



Figure 2.4. Petrographic classification of bauxites according to Valeton (1972).

#### 2.4 Bauxite Formation Mechanism

Lateritization is the process where bauxite and nickel laterite deposits are formed from the weathering of rocks. More precisely, bauxite and Fe-Ni laterite deposits in Greece share a common characteristic; both were formed as a result of lateritization and subsequent erosion of their parent rocks.

When a rock is exposed at the Earth's surface, water infiltrates though cracks and surrounds mineral crystals/grains. Hence:

- 1. Minerals are weathered.
- New minerals that are stable in the new physicochemical environment are formed instead of the destroyed minerals. The parent rock is gradually transformed into loose material (saprolite) that still maintains the basic characteristics of the parent rock.
- 3. Water is physicochemically amended, keeping in solution various elements that are released from the transformation reactions minerals.

- 4. Water is acidic and oxidizing and thus it not only dissolves minerals, but also expands cracks in the rock. This gradually leads to an increase in permeability and depth of water ingress, resulting in an expansion of the volume of material being weathered.
- 5. In case of rapid weathering, creating much more material than what can be removed by the erosion, then a "weathering mantle" remains above the parent rock that is also called regolith.

Lateritic weathering occurs in warm climates where periods of rainfall and drought alternate (tropical and subtropical climates). The intensity and the rate of lateritic weathering are mainly influenced by the nature and the mechanical characteristics of the rock, the temperature, the rainfall, the landscape morphology, the vegetation and leaching conditions (Valeton, 1972; Bárdossy, 1982). In tropical climates, high temperature increases the speed of chemical reactions, while rain facilitates the dissolution and mobility of various elements. Furthermore, vegetation, with the development and activity of root systems, contributes to the loosening of rock components. As a result its permeability increases and weathering progresses faster.

An average temperature of 26 °C, 1200-1500 mm annual rainfall and one or two months drought duration are the ideal conditions for lateritization. When rainfall exceeds 1500 mm, it is more likely that kaolinite-rich laterites will form rather than bauxite. This is because in high rainfall areas vegetation is usually dense which results in the unobstructed accumulation of plant remains. This reduces Eh values in the soil and, due to the production of humic acids, lowers its pH. Under these conditions Al and Fe remain in solution and cannot be enriched in the weathering zone (Sinitsyn, 1976).

Fe-containing minerals, such as hematite and goethite, which crystallize during periods of low rainfall, are often dissolved during rainy periods. Thus, when the dry period is long (3-4 months), the concentration of Fe minerals increases, and under these conditions iron-rich units are generally formed instead of bauxite (Bárdossy, 1982).

To sum up, the type of the parent rock, climate, landscape, water permeability and vegetation of an area control the mineralogical and chemical composition of the weathered material.

The rock resulting from the above process is called laterite (Fig. 2.5). The laterirization of aluminosilicate-rich rocks can lead to the formation of lateritic bauxite deposits. When the eroded material is accumulated specifically in karst topography it is called karst bauxite. On the other hand, nickel laterite deposits are formed through the weathering of olivine-rich rocks mainly.



Figure 2.5. Geologic cross sections of lateritic bauxite (A) and karst bauxite (B) based on field observations (Retallack, 2010).

Plagioclase is a common mineral of the feldspar group that exists in many rocks. Plagioclase is among the main rock forming minerals of volcanic rocks (like basalt and andesite) and plutonic rocks with equivalent chemical composition (such as gabbro and granite). Plagioclase also occurs in high amounts in plagioclase-rich sandstones called arkoses. When these rocks are exposed at Earth's surface, plagioclase comes to physicochemical disequilibrium with atmosphere. One common weathering reaction of sodium plagioclase (albite) is the following (hydrolysis reaction):

$$\begin{array}{c} 2\text{NaAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 2\text{HCO}_3 + 4\text{H}_4\text{SiO}_4\\ \textit{Albite} & \textit{Kaolinite} \end{array}$$

This reaction shows that albite at the Earth's surface can be weathered and gradually replaced by kaolinite. At the same time, rainwater removes the remaining products of the reaction. Kaolinite can then be transformed into an aluminum mineral, with simultaneous removal of silica. This can be described by the following reaction (Freyssinet et al., 2005):

Under specific conditions gibbsite becomes dewatered and is transformed into another aluminum hydroxide called boehmite (Tardy and Nahon, 1985):

 $\begin{array}{c} \text{AI}_2\text{O}_3.3\text{H}_2\text{O} \rightarrow \text{2AIOOH} + 2\text{H}_2\text{O} \\ \textit{Gibbsite} \qquad \textit{Boehmite} \end{array}$ 

Additionally, goethite is also dehydrated to hematite (Tardy and Nahon, 1985):

 $\begin{array}{ll} 2 FeOOH \rightarrow Fe_2O_3 + H_2O \\ \textit{Goethite} & \textit{Hematite} \end{array}$ 

Although the weathering reactions depend on the amount of water, more practically they depend on the time the reaction takes to be accomplished, which is also controlled by the morphology and the temperature of the area.

#### 2.5 Formation of Authigenic REE Minerals in Karst Bauxite

The formation of lateritic deposits including bauxites is controlled by four primary factors. In this context, the development of economic concentrations of elements in such deposits depends on a favourable conjunction of these four factors (Freyssinet et al., 2005), which are:

- 1. Parent rock characteristics (chemical and mineralogical composition)
- 2. Geomorphological conditions (location in the landscape, drainage conditions and local erosion rate)
- 3. Paleoclimatic history and
- 4. Age of lateritic weathering

In more detail, karst bauxite deposits are formed by accumulation of residual clays, derived from the weathering of aluminosilicate minerals (Freyssinet et al., 2005), in depressions on carbonate palaeotopography. The contents of the depressions are bauxitised through deep lateritic weathering and desilicification of ferrilitic soils (Gow and Lozej, 1993). 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 (Bland

and Rolls, 1998). 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 (Valeton, 1994; Mameli et al., 2007). Bauxitisation in this area occurred from the surface downwards leading to the ultimate loss of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> and accumulation of Al<sub>2</sub>O<sub>3</sub> with depth (Gow and Lozej, 1993).

Where rare earth elements 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 (Maksimović, 1976; Maksimović and Roaldset, 1976). 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 (Robb, 2005). However, the process of REE concentration is dependent on multiple factors and is still poorly understood.

Authigenic REE-bearing minerals can be formed 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. 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 (Maksimović, 1976; Maksimović and Roaldset, 1976). In order for REE minerals to develop, the initial concentration of REE adsorbed onto the clay must be greater than about 1000 ppm (Maksimović and Pantó, 1996). If the initial concentration does not reach this threshold, REE minerals are unlikely to form. 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 (Deady et al., 2014).

*Water flow:* Leaching of the bauxite by meteoric water can readily remobilise adsorbed REE (Maksimović and Pantó, 1996). Permiable 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 (Valeton et al., 1987; Valeton, 1994).
*pH:* The alkaline nature of the underlying limestone creates a high pH that results in increased stability of REE-carbonate complexes (e.g. Johannesson et al., 1995, 1996). Stability increases with atomic number, allowing HREE to be preferentially retained in solution as carbonate complexes (Mameli et al., 2007). 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 (Maksimović and Pantó, 1996).

*Fe content:* Fe-rich goethite has a significant scavenging effect, preferentially fixing mobile REE, in particular the LREE, within residual Fe-rich layers (Kühnel, 1987). Positive correlations exist between  $Fe_2O_3$  and  $\Sigma REE$ , particularly where Fe oxy-hydroxides occur as ferrigenous ooids (e.g. Mameli et al., 2007).

*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 resulting to formation of hydroxylbastnäsites for instance, which are common authigenic REE minerals in bauxite (Maksimović and Pantó, 1985).

# 3. Literature Review of Greek Bauxite Deposits and Red Mud Waste Production

#### 3.1 Introduction

This chapter presents all the bauxite occurrences in Greece and describes the geology of the Parnassus-Giona bauxite deposits, which are the most extensive in Greece and the only ones with active mining currently. Moreover, it is explained how red mud waste is produced and how it is formed from bauxite. Finally, this chapter summarises all critical metal and REE potential resources in Greece with particular focus on bauxite and red mud waste.

#### 3.2 Bauxite Occurrences in Greece

Bauxite occurs in various locations in Greece (Fig. 3.1). Identified deposits show a wide range in their size with the majority belonging to the karst type. The major bauxite deposits, occupying approximately 95% of Greek bauxite deposits, occur at Parnassus, Giona and in the Helicon mountains (central Greece). This is the sampling area of the present study, and hence more details can be found in the following sections. Minor deposits also exist in the Iti and Kallidromon mountains and in the Atalanti region, where the first (lower) bauxite horizon mainly occurs.

Furthermore, remarkable bauxite deposits occur in the Mandra-Eleusina area (Attica region). These deposits are hosted between Upper Triassic and Cenomanian limestones, are primarily composed of boehmite and have high contents of Cr, Ni, U, and Th (Papastamatiou and Maksimović, 1969).

In the Central Thessaly region (Agnanteri area), bauxite is located between Upper Cretaceous limestones and is commonly fractured. It consists mainly of diaspore with a high concentration of  $Fe_2O_3$  (29-32%) (Papastamatiou and Demiris, 1972). Other small bauxite occurrences also exist in Evia island, in Skopelos island and in the Chalkidiki peninsula (Katsika mountain).

The Skopelos bauxite is particularly interesting in terms of its genesis because it is positioned over dolomites or diabases and diabasic tuffs, and hence it is the only Greek bauxite occurrence that does not have limestone as its bedrock. However, Skopelos bauxite is not economically interesting due to its high iron content (Papastamatiou, 1963).

Gibbsitic bauxite occurrences are located in the region of Vrondero (Florina, northern Greece). These deposits that were formed by weathering of Pliocene aluminum-rich sediments, mainly occur along the contact between Tertiary and Quaternary limestones (Vgenopoulos, 1983). It is worth mentioning that the Vrondero bauxites are the only lateritic-type bauxite occurrences in Greece.



Figure 3.1. Geo-tectonic map of Greece showing the major bauxite occurrences, modified after the Geological Map of Greece (Institute of Geology and Mineral Exploration (IGME) 1983, Mountrakis (1985) and Zachariadis (2007)). The largest red circle is the location of the study area.

There are bauxite occurrences in Western Greece and specifically in Makrynoros, Klokova, Nafpaktos, Kaiafas, Smerna, Filiatra, Methoni and Pylos areas, hosted within Upper Eocene limestones (Papastavrou, 1986; Laskou, 1991, 2003). This bauxite horizon has small and less extensive deposits as the proper conditions for the bauxite formation in the Gavrovo-Tripolis zone lasted only for short duration of time.

Additionally, it is worth mentioning a few other small bauxite occurrences in Greece located in Megara area (Marmara deposit), in Othris mountain, in Pelion mountain, in Kozani area (Drepano) and in the islands of Amorgos, Naxos, Samos and Chios.

Finally, recent age bauxite formations that are developed on the surface, especially on limestone bedrocks of various ages and are composed of bauxite parts, limestone scree and red clays should also be mentioned. These secondary alluvial (placer) deposits are formed by weathering of primary deposits, are of Pleistocene age and mostly occur in Parnassus, Giona and Helicon area. These deposits are economically attractive for mining due to their relatively large size and ease of extraction, but in order to be suitable for exploitation need to be enriched in Al before undergoing the Bayer process (Economopoulou-Kyriakopoulou, 1991).

#### 3.3 Geology of the Parnassus-Giona Geotectonic Zone

The area of study is dominated by the mountains of Parnassus and Giona, and geologically belongs to the Parnassus-Giona zone, which is a part of the External Hellenides. This zone is limited only in Central Greece. It almost entirely consists of limestones and dolomites (with igneous rocks being completely absent), was obducted westwards over the Pindos zone and its main feature is the occurrence of three bauxite horizons (Fig. 3.2).

The zone is characterised by a nearly continuous sequence of epicontinental reef-like carbonates from the Upper Triassic to the Upper Cretaceous. The bauxite deposits are hosted within carbonate rocks and were formed during different geological ages. Three bauxite horizons (B1, B2 and B3) can be distinguished (from the bottom to the top), which are intercalated with shallow-water limestones, within an Upper Jurassic to Middle Cretaceous sequence. In terms of economic importance, the 3<sup>rd</sup> bauxite horizon, which was

developed as a continuous layer of 1–10 m thickness, is mostly mined (Papastavrou, S., 1986; Valeton et al., 1987; Laskou et al., 2010).



Figure 3.2. Regional distribution of the three bauxite horizons (modified after Petraschek and Mack, 1978 and Valeton et al., 1987; Anagnostou, 2010).

# 3.4 Stratigraphy of Greek Bauxite Deposits of the Parnassus-Giona Zone

The main characteristics of this zone, as described by Renz (1955), are:

- 1) A continuous sequence of carbonates generated through almost the whole of the Mesozoic
- 2) The presence of *Cladocoropsis Mirabilis Felix* fossils of Kimmeridgan age, and
- 3) Bauxite deposits that are hosted in limestones

Papastamatiou (1960) first mentioned that an important characteristic of the Parnassus-Giona zone is the continuous carbonate sedimentation starting from Upper Triassic up to the beginning of Paleocene, interrupted only by unconformities during the Jurassic and Upper Cretaceous. These discontinuities are angular and are related to bauxite formation.

The Parnassus-Giona zone stratigraphic column (Fig. 3.3) (based on Papastamatiou, 1960; Aronis et al., 1964; Papanikolaou, 1983; Katsikatsos, 1992; Kalaitzidis et al., 2010) is described below and includes:



Figure 3.3. Lithostratigraphic column of the Parnassus-Giona zone (after Katsikatsos, 1992 and Kalaitzidis et al., 2010).

**Triassic:** The presence of Upper Triassic layers firstly reported from Negris (1915, 1919). Those layers are characterized by crystalline limestones and dolomites and are structured in three groups:

- a) The lower group with no fossils
- b) The middle group with Gyroporella and
- c) The upper group with *Megalodon*

These three groups occur in their greatest extent in the southern foothills of the Giona mountain. Transitional rocks from the tectonic contact of the Parnassus-Giona and Pindos zone, which consist of clastic sediments with limestone and volcanic tuffs (Ardaens, 1978) can be observed in the area of Vardousia. These layers are Lower to Middle Triassic in age.

**Jurassic:** The Jurassic strata are very extensive and can be uniformly found in both the Giona and Parnassus areas. More precisely, these strata consist of the following series:

a) White and grey dolomitic limestones, which are over 600 meters thick

b) Dark oolitic limestones, which are approximately 200 meters thick

c) Thick-layered Lower Kimmeridgian, *Cladocoropsis Mirabilis Felix* fossils bearing limestones, which are about 300 meters thick, and

d) Tithonian limestones bearing Corals, Nerinea and Eüpsactinia.

Between b and c groups are interbedded bauxites of the first (lower) horizon. Moreover, among c and d groups occur bauxites of the second (middle) horizon, the bedrock of which is a *Cladocoropsis* bearing limestone.

**Cretaceous:** Limestone with *Corals* and *Nerinea* continued to form during the Lower and Middle Cretaceous. The limestone then becomes oolitic, with ooliths being bigger in comparison with those of the Jurassic limestone. This limestone also contains *Testaceus*, *Foraminifera* (*Miliolidae*, *Valvulinidae* and *Trocholina*) and other fossils.

In the upper layers of the oolitic limestone occurs a very thin layer of pissolitic bauxite and clays, which is reported as a "satellite bauxite layer" in the

literature (Kiskiras, 1982). The Cenomanian limestone with *Orbitolina* is placed below that layer. The limestone pack (from Tithonian to Cenomanian) is up to 400 meters thick and shows no discontinuities. Over the Cenomanian limestones occurs the bauxite of the third (upper) horizon, which was formed on an anomalous karstified surface.

All Upper Cretaceous formations lay unconformably on the Cenomanian limestone. These formations mainly consist of a thin bituminous layer of black colored micritic limestone, containing *Miliolidae*, *Charophyta*, etc. followed by a layer of micritic, *Rudists* bearing limestone of Santonian-Lower Campanian age. The thickness of these layers is approximately 100 meters.

A marine transgression took place during the Upper Cretaceous due to subsidence of the Parnassus-Giona area. Hence the sedimentation became pelagic, leading to the deposition of thin-layered, Middle Campanian-Maastrichtian limestone hosting *Globotruncana*, *Globigerina*, etc. Caminiti (1988) suggested that pelagic sedimentation did not occur over the whole Parnassus-Giona area, as believed previously (Celet 1962, Clement 1983), but that Campanian tectonism resulted in the formation of *Rudists* and *Madreporairae* hosting reefs. Those reefs are located in the areas of Giona (Kritharia) and Amfissa (Rodia). In the Rodia area especially, both of the previous formations can be observed (pelagic reefs with *Globotruncana* and reefs with *Rudists*). The Maastrichtian-Danian limit is characterized by the formation of iron-phosphate stromatolites, which mostly appear to fill cracks and fissures of rocks.

**Paleogene:** The main feature of the Paleocene-Eocene era is the buildup of clastic clayey sediments (mudstones-loam). These are also called "red line" and were gradually transformed into typical flysch of Lutetian age.

#### 3.5 Greek Karst Bauxite

Karst bauxite deposits of Greece are among the world's most important sources of non-metallurgical bauxite. There are many occurrences in Greece, formed over various geological periods in different locations. In this category though, should be added occurrences and deposits that were parts of zones, which were subducted deep in the Earth's crust and returned to the surface with different mineralogical compositions and physical properties (such as emery rocks occurring at Cyclades islands).

Exploitable deposits of bauxite exist in the regions of mounts Parnassus, Giona and Helicon (Central Greece) and the defined reserves are approximately 300 Mt (11th largest bauxite deposit worldwide). These deposits are interbedded, in the form of lenses, veins, pockets or irregular masses in limestone formations. Bauxites are related to the Mesozoic ophiolitic chains that occur along the Pindos and Vardar ocean sutured zones. These deposits are allochthonous being incorporated among various karstified limestones due to subsequent sedimentary processes (Melfos and Voudouris, 2012). The lateritic weathering zone was eroding over geological time. During periods of transgression, erosion was conduced through sea wave action (coastal erosion). The eroded material was being transferred and deposited to the foothills of the area. Later on, this material could then be further transferred as clastic material through water streams and deposited in mechanical traps that exist in the terrain. These traps are karst cavities in limestones. Cavities are created when limestones are exposed at the Earth's surface (regression of the sea). Under these conditions, limestones become relatively soluble and develop cavities or subsidences of irregular shape. Material transferred from the lateritization area as mud is then trapped in such cavities (Valeton et al. 1987; Petrascheck, 1989; Kalaitzidis et al., 2010).

When the lateritic material was completely transferred and the sea level increased, the bauxite's lateritic material was gradually covered by limestone. The occurrence of coal layers just above bauxites in some locations (Kalaitzidis et al., 2010), proves that the clastic bauxite material was deposited in a swampy environment with slightly brackish water, during the transgression of the sea (Fig. 3.4 and 3.5).

The bauxitic mud, both while dwelling in the karst and after being overlain by limestone, suffers minor mineralogical changes such as the formation of new aluminum hydroxides like boehmite and diaspore, and the formation of pyrite-marcasite (FeS<sub>2</sub>). Additionally, mobile elements (including REE) may be displaced from the upper parts (hanging wall) to the base of the deposit (footwall or bedrock).

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Figure 3.4. Lithological columns through the Pera-Lakkos bauxite deposit (Kalaitzidis et al., 2010).



Figure 3.5. Schematic sketch illustrating the depositional environment of bauxite and coal formation within the Pera-Lakkos (Giona) deposit (Kalaitzidis et al., 2010).

The allochthonous origin of the Parnassus-Giona bauxites has been proposed by various researchers (Papastamatiou 1960, Bárdossy and Mack 1967, Nia 1968). Valeton et al. (1987) suggested genetic similarities between karst bauxites and nickel laterites on karst of Central Greece. Their common model included the following phases:

- 1. Pre-lateritic alteration and reworking of ophiolites and associated rocks
- 2. Lateritic in-situ weathering, reworking and redeposition of the alteration products in an epicontinental transition environment
- 3. Post-depositional events affecting mineralogical and geochemical properties (diagenesis epigenesis)



Figure 3.6. Regional distribution of bauxites, Fe-Ni laterites and ophiolites in Central Greece. The arrows show the NE-SW transportation direction of the weathered material (modified after Biermann, 1983; Valeton et al., 1987 and Mposkos, 2007).

More precisely, for bauxite genesis, Valeton et al. (1987) suggested that the parent material of all horizons originated from serpentinites as well as from metamorphic and magmatic rocks. This was indicated by the high content of siderophile elements and lithic components. The detrital parent material was transported from a terrestrial hinterland by widely ramified river systems into a brackish lagoonal or marine environment from a northeastern to southwestern direction. Colloidal matter, fine muds and coarse material, were deposited on to a karst topography in mechanical traps by successive debris flows during cycles of emersion and marine regressions (Fig. 3.6).

Diagenesis resulted in (Valeton et al., 1987):

- a) Leaching of silica and iron under partly reducing conditions
- b) Recrystallization of iron minerals and new formation of AI minerals (boehmite and/or diaspore)

Strong supergene-epigenetic downward mobilization and reprecipitation near the footwall in chemical traps for Fe, Mn and associated elements took place during tectonic subsidence and early marine transgression. The sequences of regression and transgression during erosional, sedimentary and geochemical processes were interpreted as cyclic events.

The relation between source area and distributive province is observed particularly well in Greece. The lateritic cover of the ophiolites in the Sub-Pelagonian zone was eroded and colloids rich in iron, silica and alumina were deposited on karst in the nearby Parnassus-Giona zone (Fig. 3.7).



Figure 3.7. Relationship of source area (ophiolitic Sub-Pelagonian zone) and bauxite formation on the heights of carbonate rocks of Parnassus-Giona. a) During Early and Middle Cretaceous and b) during Early Senonian (Celet, 1962; Valeton, 1972).

The allochthonous origin of nickeliferous bauxite on karst of Jurassic limestones occurring in the Subpelagonian zone is obvious, because of the neighbouring lateritized ophiolites. Additionally, the bauxites of the Parnassus-Giona zone are characterized by high values of nickel and chromium respectively. Finally, the stratification and slight diagenetic alteration in addition to the presence of kaolinitic minerals (widely differing in lattice order), which are observed in the upper sections of the bauxite bodies, prove also that bauxites developed *in situ* from lateritic material by autochthonous diagenesis (Valeton, 1972).

# 3.6 Overview of REE and Other Critical Metals in Greece

There are many reported REE occurrences in Greece, found in various geological environments in igneous, metamorphic and sedimentary rocks of different ages (Fig. 3.8).



Figure 3.8. Overview of major REE mineralization types in Europe, Greenland and Turkey (Arvanitidis and Goodenough, 2014).

These include secondary sources such as supergene AI and Ni deposits (bauxites and laterites, central Greece), coastal heavy mineral sands (black sands) in NE Greece enriched from the weathering of neighboring igneous rocks, and phosphate limestones in western Greece. Although secondary sources are interesting in terms of economic importance and potential exploitation, there are also specific primary source occurrences that are particularly interesting such as igneous (e.g. Samothrace granite) and metamorphic rocks (e.g. ultra-mylonites and ultra-cataclastites related to the Ano Vyrsini ophiolitic complex, Eastern Rhodope) especially in northern Greece (Eliopoulos et al., 2014 and references therein).

The Parnassus-Giona bauxite is mostly (more than 70%) brown-red coloured because of the presence of iron oxides and contains approximately 57 wt.%  $AI_2O_3$  on average. Red bauxite texture is usually pelitomorphic (finegrained), ooidic (pisolitic and/or oolitic) and clastic. There are also yellow, grey and white colored bauxites (approximately 30%), which are AI enriched (>65 wt.%  $AI_2O_3$ ) and Fe depleted or "bleached". These bauxites are usually composed of diaspore (and in some cases Fe-Cr diaspore) rather than boehmite (Gamaletsos et al., 2011). Moreover, these bauxites are located along faults, their mineralogy is different compared to red bauxites and the presence of microorganisms is mainly responsible for the removal of their iron and other elements (Mariolakos et al., 1997; Laskou and Economou-Eliopoulos, 2007).

Upper Jurassic bauxite from Central Greece has 0.3  $\mu$ m average particle size (most particles range between 0.2 and 0.6  $\mu$ m) (Bárdossy and Mack 1967). Particles are nearly isometric, partly of irregular outline and partly bounded by crystal faces. On the other hand, the average particle size of the Turonian-Senonian bauxite is 1  $\mu$ m and most particles range between 0.3 to 2  $\mu$ m (Bárdossy, 1982). Particles are also isometric, but most of them are bounded by crystal faces. According to Bárdossy (1982) this is due to the difference in mineralogical constitution, as Upper Jurassic bauxite is predominantly boehmitic, whereas the Turonian-Senonian bauxite is predominantly diasporic,

The mineralogical composition of bauxites of the Parnassus-Giona Zone is: 20-50% diaspore ( $\alpha$ -AlO(OH)), 10-30% boehmite ( $\gamma$ -AlO(OH)), 20-25% haematite (Fe<sub>2</sub>O<sub>3</sub>), 1-5% kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), 1-5% calcite (CaCO<sub>3</sub>), 1-2% quartz (SiO<sub>2</sub>) and 0.5-2% anatase/rutile (TiO<sub>2</sub>) (Spoudeas, 1997; Tsirambides, 2005; Tsirambides and Filippidis, 2012). Gibbsite (Al(OH)<sub>3</sub>), goethite (FeO(OH)), illite ((K,H<sub>3</sub>O)(AI,Mg,Fe)<sub>2</sub>(Si,AI)<sub>4</sub>O<sub>10</sub>((OH)<sub>2</sub>,(H<sub>2</sub>O))), zircon (ZrSiO<sub>4</sub>), clinochlore ((Mg,Fe<sup>+2</sup>)<sub>5</sub>Al(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>8</sub>), chamosite ((Fe<sup>+2</sup>,Mg)<sub>5</sub>Al(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>8</sub>), ilmentite (FeTiO<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and pyrite/marcasite (FeS<sub>2</sub>) can be also found in smaller amounts. Furthermore, lithiophorite ((AI,Li)MnO<sub>2</sub>(OH)<sub>2</sub>) and brindleyite ((Ni,AI)<sub>3</sub>(Si,AI)<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and small chromite (Cr-spinel, FeCr<sub>2</sub>O<sub>4</sub>) fragments occur in small concentrations (Valeton, et al., 1987; Laskou, 2001; Laskou and Andreou, 2003). Kaolinite, illite and pyrite mostly occur in thrust fault affected parts of deposits (Eliopoulos et al., 2014).

REE mineral crystals are minute in size (usually less than 1 up to 10µm) and can be authigenic, detrital as a result of supergene formation in older times and in previous profiles, or can be transformed from grains derived from the weathered parent rocks (Bárdossy et al., 1976). Confirmed LREE-bearing minerals are phosphates such as detrital rhabdophane-Ce ((Ce,La)PO<sub>4</sub>·(H<sub>2</sub>O)) and florencite-Ce (CeAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), whereas, confirmed HREE-bearing minerals are Y-phosphates such as detrital churchite (YPO<sub>4</sub>·2(H<sub>2</sub>O)) and xenotime (YPO<sub>4</sub>) (Laskou and Andreou, 2003). Monazite ((Ce,La)PO<sub>4</sub>) and secondary fluorocarbonate bastnäsite/parisite-group minerals, like Ca containing hydroxylbastnäsite-Nd and La ((Nd,La)CO<sub>3</sub>(OH,F)), occur as micropore and fissure fillings (Maksimović and Pantó, 1996; Lymperopoulou, 1996; Gamaletsos et al., 2011).

Apart from the major elements, bauxite shows a wide variation in trace element compositions, including REE. Laskou and Andreou (2003) proposed that, although, Al<sub>2</sub>O<sub>3</sub> content is negatively correlated with Fe<sub>2</sub>O<sub>3</sub> (r=-0.67), it is positively correlated with  $\Sigma$ LREE (r=0.61) and  $\Sigma$ HREE (r=0.53) contents. Hence, Fe<sub>2</sub>O<sub>3</sub> is negatively correlated with REE. Additionally, TiO<sub>2</sub> is negatively correlated with MnO (r=-0.58) and REE. On the other hand, MnO increases with CaO (r=0.83), P<sub>2</sub>O<sub>5</sub> (r=0.71) and Y (r=0.55). Furthermore, The  $\Sigma$ LREE content is positively correlated with P<sub>2</sub>O<sub>5</sub>, Y, Th and U, whereas light to heavy REE (LREE/HREE) ratio is positively correlated with the Fe<sub>2</sub>O<sub>3</sub> content (Gamaletsos et al., 2011, Eliopoulos et al., 2014). Although red colored bauxites are rich in Fe, Laskou and Andreou (2003) reported that the most REE enriched bauxites were those of gray or red color, with lower Fe<sub>2</sub>O<sub>3</sub> content, higher LOI values, and higher MnO concentration. Although Th is correlated to Fe in Fe-rich bauxite, high Th concentrations appear in Fe depleted bauxite. Th is mainly contained in LREE minerals (more than 2.5 wt.% ThO<sub>2</sub> content in bastnäsite/parasite group minerals), Y-phosphates and zircon detrital crystals (Maksimović and Pantó, 1996; Laskou and Andreou, 2003; Grice et al., 2007; Gamaletsos et al., 2011). It has been recently shown that Ti-phases also host significant amounts of Th. Apart from Th, anatase grains in particular, host U and abundant Nb and Ta (Gamaletsos et al., 2011). Finally, it is known that natural zircon crystals host several elements such as Hf, Y, P, Th, U and REE (Poller et al., 2001; Crimes et al., 2007). Sc and Hf are associated with Zr, with Sc being present in the outer zone of this study's zoned zirconium crystals in bauxite (Boni et al., 2013).

Bauxite is also an important source of Ga because of the close geochemical affinity of Ga to Al enables Ga to substitute easily in rock-forming aluminosilicates such as feldspar (Burton et al., 1959). Gallium also shows an affinity with Fe and Zn, which enable it to substitute for these elements in common rock-forming minerals. Gallium can also be found in geochemical association with germanium Ge, Si, In, Cd and Sn (Burton and Culkin, 1978).

The range of Ga concentrations for bauxite deposits worldwide is <10 to 812 ppm, with an average of 57 ppm. Gallium concentrations in lateritic bauxites range from below detection (< 8 ppm) to 146 ppm; the average concentration is 57 ppm. The average Ga concentration for karst bauxite deposits is 58 ppm with a range between <10 to 180 ppm Ga. As a result, there are no substantial differences in gallium concentrations between karst and laterite-type bauxites. The range in geologically available Ga in bauxite deposits worldwide have been estimated between 30 and 82,720 metric tons (t), with an average of 14,909 t. As far as Mediterranean bauxites are concerned, Ga ranges from 5 to 812 ppm (average 53 ppm) and is estimated approximately at 1,307 t in 61 Mt of bauxite (Schulte and Foley, 2014).

Apart from the initial REE content of parent rocks, REE concentrations of bauxite deposits are controlled by the diagenetic-epigenetic modifications, the influence of circulating waters and the presence of underlying limestone chemical barriers (Maksimović et al., 1991). The two main features of REE distribution in bauxites are the enrichment *per descensum* (Fig. 3.9 and Table 3.1) and the tendency to concentrate in specific pockets, fissures and cracks.

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Figure 3.9. Downward REE enrichment at Klissura and KM 44 bauxite deposits of the  $B_3$  horizon. Samples taken from hanging wall (H) middle (M) and basement (B) of the deposits (Ochsenkühn-Petropoulou et al., 1991).

Table 3.1. Characteristic downward REE enrichment in the Mandri-Tsakni bauxite deposit of the  $B_3$  horizon (Lymperopoulou, 1996).

ppm	Hanging Wall	Footwall	ppm	Hanging Wall	Footwall
La	37	2955	Gd	13	521
Се	420	318	Dy	5.5	146
Pr	13	1025	Но	1.3	15.5
Nd	70	3843	Er	5.5	25.5
Sm	13.6	692	Yb	6	17.7
Eu	2.8	162	ΣREE	587.7	9721

The diagenesis - epigenesis stage is the key for understanding the geochemical behavior and distribution of REE in bauxites. During epigenesis, most mobile elements, including REE, re-precipitate in the lowermost parts of the bauxites, filling pore spaces. Hence, the footwall limestones act as "chemical traps" (Table 3.2 and Fig. 3.10). The intensity of epigenesis in each deposit depends mainly on factors related to groundwater mobility (Valeton et al., 1987).

Table 3.2. Epigenetic element concentration near the footwall of the  $B_2$  horizon (n=7) (Retzmann, 1985; Valeton et al., 1987).

wt.%	Min	Max	Avg	SD	ppm	Min	Max	Avg	SD	ppm	Min	Max	Avg	SD
SiO <sub>2</sub>	0.6	12.23	3.79	4.55	Ba	62	443	246	131	Zn	295	2348	1491	806
$AI_2O_3$	44.18	59.62	53.38	5.84	Co	102	2450	1442	885	Zr	2	363	76	129
Fe <sub>2</sub> O <sub>3</sub>	0.32	21.08	4.75	0.28	Cr	4	287	60	101	Y	83	371	241	89
MnO	1.91	2.99	2.34	0.36	Cu	108	632	421	227	La	67	302	2502	3305
MgO	0	0.25	0.1	0.09	Ga	0	37	8	13	Ce	270	9132	4222	3941
K₂O	0	0.65	0.14	0.24	Nb	0	42	9	15	Nd	100	4403	1263	1627
TiO <sub>2</sub>	0.01	2.2	0.4	0.8	Ni	438	3632	2465	1254					
CaO	0.18	6.86	1.31	2.46	Rb	0	18	4	7					
Na₂O	0	0.37	0.05	0.14	Sr	5	88	31	34					
P <sub>2</sub> O <sub>5</sub>	0.04	0.31	0.13	0.1	V	0	329	95	124					



Figure 3.10. Schematic diagram showing the typical classic Mediterranean type karst bauxite (Bárdossy, 1982; Deady et al., 2014).

REE mobility is based on leaching by percolating pore waters. LREE are removed under acidic conditions, while HREE are preferentially removed under alkaline and weakly alkaline conditions, respectively. The deposition environment is determined by the La/Y ratio. More specifically, when the La/Y ratio in absolute values is lower than 1, the deposition environment is acidic and when the former is higher than 1, the latter is alkaline respectively (Crnicki and Jurkovic, 1990). Hence, the higher La/Y ratios occur in the lower parts of the karst bauxite deposits (Maksimović et al., 1991). Furthermore, if the La/Lu, La/Y and  $\Sigma$ LREE/ $\Sigma$ HREE ratios have their highest values in the base of the deposit, this is possibly a reworked multistage bauxite deposit (Laskou and Andreou, 2003).

Table 3	.3. Compariso	on of average	e major	and	trace	element	values	of the	three
bauxite	horizons (Ecc	nomopoulou	-Kyriak	opoul	ou, 19	991).			

wt.%	B1	B2	B3	Correlations	ррт	B1	B2	B3	Correlations
$AI_2O_3$	52,94	53,60	58,55	1st<2nd<3rd	Ni	242	340	598	
Fe <sub>2</sub> O <sub>3</sub>	23,68	22,23	22,98	2nd<3rd<1st	Со	35	37	38	1ct_2nd_2rd
TiO <sub>2</sub>	2,43	2,26	2,67	2nd<1st<3rd Pb		67	72	125	151<2110<510
SiO <sub>2</sub>	6,68	6,82	2,52	3rd<1st<2nd	V	319	505	724	
CaO	0,27	0,39	0,17	3rd<1st<2nd	Р	481	427	413	
					Zn	235	190	52	1st<2nd<3rd
					K	715	1187	298	
					Mn	142	907	100	
					Sr	91	114	71	3rd<1st<2nd
					Y	87	124	64	
					Zr	514	506	560	2nd +1 ot +2rd
					Cr	450	379	1079	2110<151<510
					Ga	64	59	60	2nd<3rd<1st

The main issue in REE exploitation from bauxites is their heterogeneity due to the aforementioned reasons. This is displayed within single mines, both in single horizons and between horizons (Table 3.3). Therefore, it is very difficult to estimate a representative  $\Sigma$ REE value, which is problematic when attempting to estimate grade and tonnage of REE from bauxites or their byproducts. Tsirambides and Filippidis (2012) reported that the REE contents of bauxites and lateritic bauxites of Central Greece range from 3275 to 6378 ppm, while Laskou and Andreou (2003) suggested a range from 458 to 2319 ppm in two mines of the 2<sup>nd</sup> and 3<sup>rd</sup> bauxite horizon (Fig. 3.11).



Figure 3.11. Map of Greece showing REE concentrations of various deposits (modified after Tzerefis, 2012 and Arvanitidis et al., 2013).

Furthermore, Ochsenkühn-Petropoulou et al. (1994) suggested that  $\Sigma$ REE in mixed bauxite extracted from various mines (mainly from B3 and sometimes from B2 horizon) of the Aluminium S.A. plant was 560 ppm and  $\Sigma$ REE in the corresponding red mud is 1040 ppm. 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.

Table 3.4. Average composition of bauxite (B1, B2, B3 and BP) and red mud (RM). Data are from Valeton et al., 1987; Ochsenkühn-Petropoulou et al., 1991; Economopoulou-Kyriakopoulou, 1991; Ochsenkühn-Petropoulou et al., 1994; Ochsenkühn et al., 1995; Laskou and Andreou, 2003; Laskou, 2005; Laskou and Economou-Eliopoulos, 2007; Laskou et al., 2010; Laskou and Economou-Eliopoulos, 2013 and data kindly provided from Delphi-Distomon S.A. and Aluminium S.A.

wt.%	B1	B2	B3	BP	RM		B1	B2	B3	BP	RM
SiO <sub>2</sub>	7.7	8.3	3.1								
Al <sub>2</sub> O <sub>3</sub>	59.3	53.9	55.6								
Fe <sub>2</sub> O <sub>3</sub>	15.2	19.1	22.1								
MnO	0.1	0.2	0.1								
MgO	0.1	0.3	0.1								
CaO	0.6	1.1	0.3								
Na₂O	0.7	0.1	0.1								
K <sub>2</sub> O	0.5	0.6	0.4								
TiO <sub>2</sub>	3.1	2.3	2.3								
P <sub>2</sub> O <sub>5</sub>	0.1	0.1	0.1								
LOI	12.3	14.1	14.8								
ррт											
Ag			0.7			Sc	62.3	50.0	37.0	59.4	119.4
As			156.8		115.0	Y	44.4	159.1	48.0	55.4	93.1
Ва	83.3	72.0	130.5			La	54.5	258.4	64.1	80.2	150.6
Be			3.3			Ce	178.0	427.5	195.0	259.6	421.6
Bi			4.8			Pr	11.5	43.0	7.9	13.8	25.6
Cd			1.3			Nd	62.3	149.2	60.4	59.9	120.9
Co	37.5	62.5	37.3			Sm	8.4	57.2	7.4	13.8	29.1
Cr	437.4	346.3	986.0		1500.0	Eu	2.0	13.0	1.9	2.9	5.0
Cu	59.0	99.4	14.0		36.0	Gd	7.2	61.0	7.1	12.5	23.3
Ga	60.0	46.5	50.0	70.0		Tb	1.1	8.7	1.8	1.3	
Ge						Dy	6.9	46.9	8.2	7.0	14.4
Hf			22.2			Но	1.4	9.2	1.9	2.2	4.3
Мо			30.0			Er	4.1	23.5	5.7	8.1	17.2
Nb	85.0	43.7	46.0			Tm	0.5	3.3	1.0	1.3	
Ni	229.4	296.2	530.5		700.0	Yb	4.3	19.0	6.1	7.4	15.6
Pb	67.0	72.0	85.1			Lu	0.7	2.7	0.9	1.4	2.4
Rb	5.0	18.0	8.3			ΣREE+Sc+Y	449.6	1331.7	454.4	586.2	1042.5
Sb			20.3								
Sr	76.0	101.0	36.5		120.0						
Та			3.5								
Th			43.0	42.4							
U			9.7	7.3							
V	350.4	375.3	545.9		800.0						
W			46.3								
Zn	191.8	319.3	73.9		40.0						
Zr	813.0	435.8	556.8								

For these reasons, there was an attempt to carry out a review of published REE values for Greek bauxites (from all three horizons), excluding papers that present high REE values from specific positions. Also, average values were estimated for samples of mixed throughput ore from the Aluminium S.A. plant, gathered from several mainly B3 and sometimes B2 mines for alumina production. Finally, the average concentration of dehydrated red mud waste was estimated, which is the byproduct of mixed bauxite after the Bayer process. Table 3.4 summarises the average major and trace element concentrations reviewed from the literature, while Figure 3.12 projects the REE chondrite normalized values of the three bauxite horizons (B1-B3), mixed bauxite of the Aluminium S.A. plant and the correlated red mud waste.



Figure 3.12. Plot of average published REE values for each of the three main bauxite horizons (B1, B2 and B3), mixed bauxite ore that enters the Aluminium S.A. plant (BP) and dehydrated red mud waste (RM). All values are chondrite normalized using McDonough and Sun (1995).

REE concentrations in the collated data indicate variation across the three main bauxite horizons, with a mixture of these horizons entering the processing plant (BP). The two-fold increase in REE in the red muds compared with the original bauxites is consistent with the literature (e.g. Ochsenkühn-Petropoulou et al., 1994). 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 illustrates the need for a robust sampling strategy involving the collection of more carefully characterized samples.

#### 3.7 Red Mud Waste

The universal industrial practice for the production of high-grade metallurgical alumina ( $Al_2O_3$ ) is the Bayer process (Fig. 3.13). The solid waste produced by this is known as red mud. During the Bayer process, bauxite is digested (leached) in a solution of sodium hydroxide NaOH at high temperature and under pressure in autoclaves. The temperature ranges from 145 to 260°C, depending on the bauxite grade. Aluminium oxides, after liquid-solid separation, are received in solution for further treatment for alumina production (precipitation and calcination). The remaining solid red mud, after several washings, is taken up as a suspension (slurry) and discarded.



Figure 3.13. Outline of the Bayer process for alumina production (www.alteoalumina.com).

Red mud contains many useful components such as un-dissolved  $AI_2O_3$ ,  $Fe_2O_3$ ,  $TiO_2$ ,  $SiO_2$ ,  $Na_2O$  etc., but as a waste product can also represent a serious environmental hazard, either if it is deposited in inactive mines (as usually happens in the USA and Japan) or when it is discarded in the sea, as in

many cases in Europe. In Greece before 2007, red mud was disposed of in the sea, but since has been placed into stockpiles near the Aluminium S.A. plant (Fig. 3.14).



Figure 3.14. Red mud waste stockpiles at the Aluminium S.A. plant.

Red mud production depends on the bauxite composition, but it is estimated that about 1.06 t of red mud is created for each 1 t of alumina produced. The actual composition of red mud depends on the type of bauxite, the mining location and the parameters set for the Bayer process. The waste is primarily composed of iron oxides in the form of hematite (Fe<sub>2</sub>O<sub>3</sub>) and maghemite (y-Fe<sub>2</sub>O<sub>3</sub>), aluminium oxides in the form of diaspore ( $\alpha$ -AlO(OH)) and gibbsite  $(AI(OH)_3)$ , and silicon, calcium, sodium and titanium oxides such perovskite  $(CaTiO_3)$ , rutile as calcite  $(CaCO_3)$ .  $(TiO_2)$ , cancrinite (Na<sub>6</sub>Ca<sub>2</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>(CO<sub>3</sub>)<sub>2</sub>.2H<sub>2</sub>O), quartz (SiO<sub>2</sub>) and silicon calcium aluminate hydroxide  $(Ca_3AI_2(SiO_4)(OH)_8)$ .

Besides the main elements, red mud contains a wide variety of trace elements. Generally, the major and trace element composition of both bauxite and red mud vary according to the bauxite mining location. Moreover, concentrations of elements such as Cr, Ni, REE, V and Zr vary and occasionally occur in high concentrations in some bauxites, from several hundred up to a few million ppm (Maksimović and Papastamatiou, 1973; Valeton et al. 1987; Papastravrou and Perdikatsis 1987; Petrascheck, 1989; Economopoulou-Kyriakopoulou, 1991; Laskou, 2005; Laskou and Economou-Eliopoulos, 2007; Laskou et al., 2010; Laskou and Economou-Eliopoulos, 2013). Red mud trace element concentrations show that these elements pass through the Bayer process and thus appear to be enriched (Ochsenkühn-Petropoulou, et al., 1994; Laskou and Economou-Eliopoulos, 2013). The trace elements may include those considered "critical" such as Be, Co, Ga, Ge, Mg, Nb, REE including Sc and Y, Sb, Ta and W (Table 3.4 and Tables in Chapter 6). As a result, bauxite and red mud can be used as an important alternative source for exploiting those elements.

Although the elements mentioned above are expected to be concentrated during formation of bauxites, simultaneously elements like Ba, Ca, Mg and Sr tend to be removed. This phenomenon does not seem to apply to La for instance, because of its ionic and atomic properties that have a key role in its distribution. An important criterion for the distribution of elements is the ionic charge to radius ratio (ionic potential). Elements, for which this ratio has a low value, remain in the ionic solution during weathering of rocks. Those of medium ratio precipitate through hydrolysis and their ions tend to bind to hydroxyl radicals, while those with high ratio form soluble anionic complexes. Therefore, it seems that elements concentrated into bauxite are those with an ionic charge (Z) to ionic radius (r) ratio in the range from 3 to 9.5 (Lymperopoulou, 1996) (Table 3.5).

Table 3.5.	lonic charge	(Z) to ioni	c radius (r)	ratio in	some elem	nents (Taylo	r and
Eggleton,	2001).						

Element	Z/r	Element	Z/r	Element	Z/r
Cs⁺	0.6	Zn <sup>+2</sup>	2.4	U <sup>+4</sup>	4.1
K⁺	0.7	Mg <sup>+2</sup>	2.5	Ga <sup>+3</sup>	4.2
Na⁺	0.9	Cu <sup>+2</sup>	2.5	V <sup>+3</sup>	4.2
Ba <sup>+2</sup>	1.4	La <sup>+3</sup>	2.6	Cr <sup>+3</sup>	4.3
Pb <sup>+2</sup>	1.6	Ce <sup>+3</sup>	2.6	Ce⁺⁴	4.6
Sr <sup>+2</sup>	1.7	Bi <sup>+3</sup>	2.7	Al <sup>+3</sup>	4.9
Ca <sup>+2</sup>	1.9	Ni <sup>+2</sup>	2.9	Sn⁺ <sup>4</sup>	5.2
Cd <sup>+2</sup>	1.9	Y <sup>+3</sup>	2.9	Zr <sup>+4</sup>	5.6
Mn <sup>+2</sup>	2.2	Sc⁺ <sup>3</sup>	3.4	Be <sup>+2</sup>	5.7
Fe <sup>+2</sup>	2.3	Th <sup>+4</sup>	3.4	Ti <sup>+4</sup>	5.8
Co <sup>+2</sup>	2.4	Fe <sup>+3</sup>	4.1	Mn <sup>+4</sup>	6.5

Most important is the fact that almost all trace elements in bauxite are partitioned into the red mud, with exception of Ga and probably the Be. 100% of REE in particular pass into the red mud. The average concentration of REEs including Sc and Y in Greek bauxite is about 500 ppm, whereas the average concentration in red mud is approximately 1000 ppm. The enrichment factor of REEs, including Sc and Y, in red muds compared to the initial bauxite is 2:1 (Ochsenkühn-Petropoulou et al., 1994).

# 4. Field Sampling

#### 4.1 Introduction

This chapter describes the sampling process followed for collecting bauxite and red mud waste samples. Additionally, it includes a geological map that has been designed for this thesis and illustrates the underground bauxite mines (sampling positions) in relation to their host rocks.

#### 4.2 Sampling Details

Bauxite and red mud waste sampling was carried out during 16 October and 4 November 2013. Fifty five samples (37 bauxite and 18 red mud waste) were collected in total, weighing approximately 240 kg. Bauxite was sampled from recently started underground mines of the Delphi-Distomon mining company, (subsidiary of Aluminium S.A.), whereas red mud waste samples were taken from Aluminium S.A. stockpiles of dehydrated red mud, deposited after the Bayer process.

Four underground mines which operate within the 3<sup>rd</sup> bauxite horizon were sampled: Vargiani, Silas, Gouves and Spartolakka (Fig. 4.1). The thirty seven bauxite samples each weighed more than 5 kg and were taken from two sampling positions within each mine, which gave eight sampling spots. Sampling was carried out vertically in all profiles and the number of samples taken depended on the height of each profile. Four or five almost equidistant samples were collected from each profile. Bauxite sampling details are summarized in Table 4.1. Additionally, the geological map and the columnar section of the sampling area are shown on figures 34 and 35 respectively.

Mine	Varg	giani	Si	as	Go	uves	Spart	tolakka
Profile	1	2	1	2	1	2	1	2
Hanging Wall	577 m	571.5 m	516 m	500 m	307 m	309 m	236 m	245.5 m
Footwall	572.5 m	566 m	508.5 m	490.5 m	301 m	304.5 m	230 m	239.5 m
Profile Height	4.5 m	5.5 m	7.5 m	9.5 m	6 m	4.5 m	6 m	6 m
Samples Collected	4	4	5	5	5	4	5	5
Total Depth Sampled	11	m	25.	5 m	8	ßm	15	.5 m
Unsampled Depth	1	m	8.5	5 m	C	) m	3.	5 m

Table 4.1. Details of sampling positions in each mine.



Figure 4.1. Geological map of the sampling area also projecting the mines sampled (modified after Papastamatiou et al., 1960 and Delphi-Distomon S.A. maps).

The legend of the geological map above (Fig. 4.1) includes the following formations:

# Holocene (Alluvium)

AI: Recent alluvial deposits.

AISc: Colluvial deposits. Talus and slope fan debris.

**Bsec**: Secondary bauxite deposits. Pebbles and gravel of bauxite in an argilaceous matrix.

# Pleistocene (Diluvium)

DI: Torrential conglomerate. Pebbles mainly of limestone. Fluviatil terrace 5-8m.

# Parnassus-Giona Series

**Fp**: Undivided flysch. Its layers from the earlier to the more recent include: a) reddish calcareous shale with a characteristic columnar jointing. Thickness 50-70m. b) sandstone and c) conglomerate. Limestone lenticular intercalations in the upper layers are developed, usually containing clastic material. The deposition of this complex began from Paleocene.

**Fpc**: Conglomerate in the upper layers of the flysch, of low cohesion, with intercalations of sandstone. Pebbles of limestone, serpentine, granite, diorite, hornstone and flysch material. Thickness 20-30m.

**K8-e**: Thin-bedded limestone, concretionary in the upper layers. It is compact, of white brown color, sometimes reddish, greenish or yellowish with nodules of chert (Senoninan - Paleocene). Thickness 50-70m. It is underlying, in conformity, the reddish shale of flysch complex and overlying, in conformity also, the limestone with *Rudistae*.

**K7-8**: Compact or microcrystalline limestone of gray or dark gray color, with a bituminous odour when crushed. In the upper layers it falls into a white crystalline limestone characterized by *Rudistae* fragments. This limestone is the hanging wall of the upper bauxite horizon. Thickness 80m (Turonian–Denonian).

**K7-e**: Undivided upper cretaceous limestone. The limestone (K7-8) and (K8-e) are here included. Total thickness about 150m.

**B3**: Bauxite of the upper horizon. Usually reddish or brownish in color, pissolitic, mostly containing diaspore. Rarely white and then rich in alluminium. Footwall contact of irregular shape.

**B3und**: Underground deposits of the B3 horizon.

**J13-K6**: Intermediate limestone. It is developed between the upper and lower bauxite horizon. Blocky or thin-bedded. Usually microcrystalline of a white color, immediately below the bauxite of the upper horizon, containing fossils. The lower strata in contact with bauxite of the lower horizon are reddish, marly limestone of concretionary structure, containing fossils (Tithonian). Typical oolitic limestone is developed in the upper layers (Cenomanian) in the middle of this calcareous series. Total thickness is about 400m.

**J1-11**: Jurassic limestone with similar microscopic lithological characteristics as the intermediate limestone (J13-K6). It is developed below the *Cladocoropsis* containing layers. Dark colored, compact or crystalline sometimes, with oolitic structure in the upper layers, containing gastropods and bivalves in the middle and lower layers as well as *Pinidae* in the last ones.

Ki: Undivided Mesozoic limestone, mainly of lower Cretaceous age.

# **Overthrust Eastern Greece series**

Middle and upper Cretaceous formations of Eastern Greece overthrust on Parnassus-Giona zone. They are composed of:

**K6f**: Flysch-like rocks (marly platy limestone and a series of clay – sandstone of low cohesion, containing spearly pebbles mainly of serpentine and red chert), in which lenses of limestone included.

K6: Cenomanian overlap.

**K5**: Crystalline limestone with fragments of *Rudistae*, containing small pieces of red chert alternating with compact limestone with *Globotruncana sp.* Over this formation lays compact limestone with *Globotruncana sp.* and subsequently limestone with *Orbotoidae*. Turonian-Maestrichtian.

The 1:90,000 geological map of Figure 4.1 was created by combining the Amfissa geological map (sheet number 171, scale 1:50,000) of the Institute Geology and Mineral Exploration (IGME) (Papastamatiou et al., 1960) and the 1:20,000 geological map of the mining area kindly provided by Delphi-Distomon

mining company, created by their geologists in October 1998. This map was designed by using ArcMap 10 software of ESRI's ArcInfo/ArcGIS suite. Moreover, the columnar section of the area of study (Fig. 4.2) was modified after the Amfissa geological map of IGME.

Quaternary	07 00 00 00 000	Alluvial and secondary bauxite deposits
Pliocene	000000000000000000000000000000000000000	
Unconformity	To us a o otto	Conglomerate with calcareous intercalations
	and the second state of th	Flysch - Sandstone
Focene	and the second second second	Reddish shale
Loccie		
		-
	The Part of the Pa	
Paleocene	for the start of t	Light colored limestone
		Compact light colored limestone with Globotrucana
	0 9 0 8 0	
	that a latera	White crystalline limestone with fragments of Rudistae
Upper Cretaceous	H- I- I- I- II	
		Dark colored limestone with Rudistan
Ang Unconformity		3 <sup>rd</sup> hauxite horizon
Cenomanian		White microcrystalline limestone
Cenomaman	TTTT	while interocrystalline intestone
	000000000	
	10101010101	
Lower Cretaceous	and the second	Gray collitic limestone with gastropods and arguacous bauxitic material
	0 0 0 0 0 0 10	
	1.1.1.1.	
Tithonian		Limestone with Nerinea and Ellipsactinia
		-
Ang Unconformity		Marly concretionary reddish limestone with Nerinea
Unner Jurassic		2 <sup>nd</sup> bauxite horizon
(Kimmerdgian)	TATT	Dark colored limestone with Cladocoronsis
(Isimmerugian)	TETT	Dark colored innesione with Chanocoropsis
		a dia manana
		1 <sup>°°</sup> bauxite honzon
	1 1 1 1 TOT	
Lower Jurassic	0 0 0 0	Oolitic limestone
	0 0 0 0	
	La	Grav colored limestone with Pinidae
	1 TUNIN	
Unner Triaccio	5/11/11/	Dolomite dolomitic limestone or limestone with Magaladan
opper massic		Givenovalla and Carola
	N/ N/	Gyroporena and Corais
	VIVIII K	
	t the history	

Figure 4.2. Columnar section of the Parnassus-Giona geotectonic zone (modified after Papastamatiou et al., 1960).

Bauxite characteristics slightly differ with location. Variations in color (chemical composition), texture, tenacity and hardness are macroscopically easy to observe with naked eye. Moreover, it is obvious that micro-tectonics are also responsible for changing the chemistry of the bauxite. Different minerals occur in cracks and veins and were formed by filling empty spaces. The occurrence of AI enriched and Fe depleted veins of white bauxite are the most common in almost all bauxite mines.



Figure 4.3. Variation in color, texture, tenacity and hardness of bauxite at an underground bauxite pillar sampled.

Figures 4.3 and 4.4 show bauxite's color variation, from typical red to brown (Fe-rich), yellowish and whitish (Al-rich). These pictures were captured during the period of sampling from various underground mines. Because of the high profiles in the underground bauxite deposits, sampling was carried out by using underground lift vehicles and loaders, kindly provided by Delphi-Distomon mining company. Height measurements were made by a laser distance meter, while distance between the sampling points was measured by using a metre.



Figure 4.4. Typical red bauxite in an underground mine during sampling.

Red mud waste samples were collected from dehydrated red mud waste stockpiles of Aluminium S.A. located near the company's plant in Agios Nikolaos, Greece (Fig. 4.5). Red mud waste is deposited subsequently after bauxite has come through Bayer process. Bauxite originates from various Parnassus-Giona bauxite mines mainly of the 3<sup>rd</sup> horizon and a few of the 2<sup>nd</sup> one. Mixed bauxite is stored in the Aluminium S.A. plant and then is used blended with the addition of small amounts of imported tropical bauxite for the Bayer process. The residue is deposited in dehydrated form near the plant. The deposition was started in 2009 and before that red mud waste was discarded into the sea.

For waste disposal purposes the company has developed plateaus right near the plant. Seven plateaus (A to H) in different positions exist today, where A is the older one and H is the most recent (Fig. 4.6). Each plateau represents red mud waste that came from different bauxite deposits and passed through the Bayer process and deposited at different periods of time. The company is scheduled to mix all the red mud waste plateaus in the near future and redeposit them on one plateau, the material of which will be potentially used for red mud waste exploitation such as rare earth element and other critical metals extraction.



Figure 4.5. Google Earth satellite map of the sampling area. Red pins project the locations of underground Delphi-Distomon bauxite mines sampled. Brown pin shows the Aluminium S.A. plant location, where red mud waste samples were collected.



Figure 4.6. Red mud waste deposition plateaus during sampling.



Figure 4.7. Red mud waste variation in cohesion. Cohesive and loose red mud waste during sampling on the left and right pictures respectively.

Eighteen samples of red mud waste were collected from three plateaus (A, B and Z), weighing approximately 1.5 kg each. These samples came out of

five different profiles, one from plateau A, one from plateau B and three from plateau Z. Most of the plateaus are inclined and very high. Despite that, plateau Z was divided into three sub plateaus at different levels (the higher, the middle and the lower part), therefore it was feasible to access three different sampling levels. Red mud waste samples were vertically collected; all spots in every profile were equidistant. Profile height and distance between the sampling spots were measured in metres. Samples were collected with a shovel and were coned and quartered *in situ*, before the final sample was sealed into a plastic bag (Fig. 4.7 and 4.8).



Figure 4.8. Aluminium S.A. high and inclined red mud waste plateaus during sampling.

Red mud waste was deposited homogeneously onto the plateaus. However, a slight graduation in cohension was observed with the naked eye, with red mud waste's cohension increasing with depth. This variation is most likely related to the pressure applied by the weight of the overlying material. Hence, red mud waste in the base of the plateau is relatively more compressed compared to the recently deposited loose material in the upper parts of the plateau. Additionally, white grains that are usually very hard can be observed in red mud waste. These grains are remnants of materials used in calcination during the Bayer process. Red mud waste sampling summary is shown in the following table (Table 4.2).

Profile	Plateau A	Plateau B	Plateau Z Profile A (Upper)	Plateau Z Profile B (Middle)	Plateau Z Profile C (Lower)
Profile Height Sampled	3 m	3 m	2 m	2 m	3 m
Samples Collected	4	4	3	3	4

Table 4.2. Details of red mud waste sampling positions.

# 5. Methodology

# 5.1 Introduction

This chapter presents the sample preparation techniques and methodologies used for analysing bauxite and red mud waste samples. More precisely, X-ray diffraction (XRD) method was used for identifying the major mineralogy, while X-ray fluorescence (XRF) and inductively coupled plasmamass spectrometry (ICP-MS) analysis were used for the whole rock compositions. Particular attention is given on the difficulties on dissolving the samples for the trace element analysis and the various techniques that were tried in order to find the most suitable method. Regarding optical microscopy and electron beam techniques, reflected and transmitted light microscope, scanning electron microscope (SEM) and electron probe microanalyser (EPMA) were used for identifying the main, secondary and REE minerals. Finally, this chapter reviews published leaching methods for REE and suggests a new stepwise REE leaching protocol (CSM protocol) for various weathered REE rich rocks and their by-products.

# **5.2 Sample Preparation**

Approximately 240 kg of bauxite and red mud waste samples were used for the whole rock composition analysis (Fig. 5.1).

# Bauxite sample preparation:

- Each bulk rock sample (≥5 kg) was divided into two equal parts. Additionally, one duplicate sample was made from one random sample from each profile (M1 S3, M1 S6, M2 S3, M2 S8, M3 S4, M3 S9, M4 S1 and M4 S10).
- 2. The first part was used for X-ray diffraction and whole rock composition analysis, while the rest of the sample was kept as archive and for creating thin polished sections and polished blocks.
- The first part was crushed down to ≤1mm using a Fritsch "Pulverisette 1" Model II jaw-crusher.
- 4. From every crushed sample one duplicate was prepared.
- 5. Some polished blocks were made from that material as well.
- The crushed sample was riffled down to ≤100 g, while the remaining sample was stored as archive.
- 7. Approximately 50 g of the sample were ground for 5-10 minutes in a Tema Tungsten Carbide ring mill. This produced around 40 g of pulverized sample passing a 200 mesh (<75 microns). The powdered samples were contaminated with W from the Tema.
- 8. To avoid possible contamination between samples, each apparatus used for sample preparation was cleaned carefully with ethanol each time used. Additionally, for removing the iron oxides from the ring mill, the Tema was run with a charge of ground Cornish granite and one run with beach sand between each bauxite sample.



Figure 5.1. Laboratory flow diagram for the analysis of bauxite samples.

Red mud waste sample preparation:

- 1. The coning and quartering method was used for the red mud waste samples during field sampling.
- In the laboratory, each sample (weighing more than 1.5 kg) was coned and quartered again down to ≤100 g. The remaining sample was stored as archive.
- Each sample was ground to <75 microns (able to pass a 200 mesh) by using an agate mortar.
- 4. Again every tool including the agate mortar was carefully cleaned between each sample to avoid potential contamination.

# 5.3 X-ray Diffraction Method

All bauxite samples were first ground in a tungsten carbide Tema mill, and then about 15-20 g of each sample was ground again by hand using an agate mortar and pestle, in order to ensure a particle size of <100  $\mu$ m. The fine powdered samples were then pressed into powder holders and analysed on a Siemens D5000 X-Ray diffractometer (Cu K $\alpha$  radiation, 40 kV and 30 mA) at Camborne School of Mines, University of Exeter. Samples were typically scanned at room temperature over angles of 2° to 70° 2q, on a 0.02° step with a step time of 1 second, taking about 1 hour. Samples were rotated during measurement to minimize the effects of preferential mineral orientation. The profiles produced by the scans were later interpreted to match peaks with known mineral markers using the JCPDS PDF-2 (2004) database and EVA software V.10.0.1.0. Detection limits are approximately of the order of 3 to 5 weight %, but this is mineral and sample dependent.

## 5.4 X-ray Fluorescence Analysis

Eight random bauxite samples (one from each profile or two from each mine) were selected for major, minor and trace element analysis, using a Bruker S4 Pioneer XRF, type WD-XRF at Camborne School of Mines, University of Exeter. Samples were prepared as 15 g pressed powder pellets and run semiquantitatively, in order to get a first picture of the chemical composition and especially to determine the content of minor, trace and REE.

For the XRF major, minor and trace element compositions of red mud waste, three samples (one of each deposition plateau) were again randomly selected. Red mud waste samples were treated, prepared and analysed with exactly the same way as the bauxite samples.

The standardless (semi-quantitative) analysis is generally applied by performing upon a sample a qualitative scan with peak identification, then utilising the fundamental parameters (FP) method to relate measured and theoretical intensities of detected elements and perform inter-element corrections. When the determination of sample chemistry is made, the loss on ignition (LOI) value is added into the sample chemistry using the analysis software. Data from this analysis were mainly used to determine approximately the levels of different elements before the ICP-MS analysis in order to plan the calibration.

More precisely, each dried and ground sample was mixed with 2.5 mL of a solution of Elvacite 2013 resin dissolved in acetone (200 g/L) in an agate pestle and mortar until a dry powder remains. This was loaded into a steelpressing die (40 mm diameter) and then boric acid ( $H_3BO_3$ ) was added as a backing material. The pellet was pressed in a Moore hydraulic press at 20 tonnes for 60 seconds and then was ejected from the die.

For the LOI calculation, approximately 2g of each dried and ground sample was placed into a pre-fired platinum crucible (previously weighed to 4 decimal places) and precisely weighed to 4 d.p. All samples were ignited in a kiln at 1000°C for a minimum of 60 minutes. Then, samples were removed from the kiln and allowed to cool in a desiccator, before re-weighing a final time to 4 d.p. In order to be sure of the total evaporation of all volatiles, samples were ignited again for one additional hour, but and no difference in weight was observed. The samples were cooled again under moisture-free conditions (desiccator vessel). The formula used for the estimation of the loss on ignition is:

 $w_{C=}$  Crucible weight  $w_{C+S=}$  Crucible+Sample weight  $w_{Ian=}$  Weight after Ignition  $LOI\% = [(w_{C+S}-w_{Ign})/(w_{C+S}-w_{C})] \times 100$ *i.e.* mass lost / mass of original sample, as a percentage

# 5.5 Inductively Coupled Plasma-Mass Spectrometry Analysis

Quantitative analysis of bauxite and red mud waste samples for trace and rare earth elements was carried out using the Agilent 7700 Series ICP-MS within the CSM analytical laboratory and the ICP-MS of ACME Labs, Canada, respectively. BX-N of ANRT (Association Nationale de la Recherche Technique) was selected as a certified standard reference material for crosschecking the success of the process (Fig. 10.21). Additionally, ACME labs also used the STD SO-18 as a standard reference material. Moreover, blank and duplicate samples (apart from the sampling duplicates) were used in each analysis run for quality control and for checking potential contamination between samples. Every batch (24 slot sample holder) contained two reference material samples and two blanks. Finally, due to the fact that there were not applied any corrections to the ICP-MS data produced by CSM or ACME laboratories, some elements such as Ba and REE may interfere.

# 5.5.1 Dilution Methods - Results for Bauxite and Red Mud Waste Samples

The first ICP-MS analysis at CSM was done by the following procedure. Bauxite and red mud waste powdered samples were prepared (dissolved and diluted into solution) by using the CSM 4 acid digestion protocol, which is a mixture of concentrated hydrofluoric (HF), hydrochloric (HCl), nitric (HNO<sub>3</sub>) and perchloric (HClO<sub>4</sub>) acids. Bauxite, red mud waste and reference material samples underwent all of the following steps.

**Digestion process:** 

- 250 mg of each sample was weighed out accurately into 50 ml screw cap Teflon digestion vessels.
- Sample was rinsed from the sidewalls of Teflon vessel with a minimum of DI water.
- 3. 4 ml of HF (47-51% Fisher Tracemetal grade) was carefully added and then allowed any reaction to subside.
- 3 ml of conc. HCl (Fisher Tracemetal grade) was added and followed by 1ml of HNO<sub>3</sub> (Fisher Tracemetal grade). Again there was some time given to allow any reaction to subside.

- Sample vessels were sealed lightly by replacing the cap before being placed in DigiPrep digestion block pre-set. Samples were left on the digestion block overnight (more than 8 hours) at 160 °C.
- 6. Teflon vessels were removed from the digestion block and allowed to cool.
- 7. The cap of each sample was removed and then 1 ml of  $HCIO_4$  (VWR Normatom 65%) was added.
- The samples were returned to the digestion block and taken to incipient dryness at 180 °C.
- Once dry, the samples were removed again from the digestion block, allowed to cool and a further 1 ml of HNO<sub>3</sub> (Fisher Tracemetal grade) was added to each sample.
- 10. After that, samples were returned to the digestion block and taken again to incipient dryness at 180 °C.
- 11. Samples were again removed from the digestion block, allowed to cool and a further 1 ml of conc. HNO<sub>3</sub> and 5ml of de-ionized water were added this time.
- 12. Then, vessels were capped and warmed gently in the digestion block set at 100 °C for 30 minutes.
- 13. Samples were removed from heat and allowed to cool, followed by adding 44ml of de-ionized water and shaking well in order to mix.
- 14. Finally, each sample was transferred to a 50 ml polypropylene sample container.

# Dilution process:

- 1. Each sample was diluted into a 1:100 by taking 0.5 ml of sample solution and diluting with 49.5 ml 5% HNO<sub>3</sub>.
- Samples were placed in polypropylene sample tubes (QMx DigiPrep) and capped for analysis.
- Additionally, reagent blanks (n=3) were carried out alongside the samples during every digest batch to assess potential elemental contamination.
- Finally, a suitable certified standard reference material (BX-N of ANRT) was also used and underwent to all previous digestion and dilution stages.

However, total dissolution of samples was not achieved. Residue remained, sticking in the sides and bottom of the Teflon vessels. Residue was greater for bauxite than for the red mud waste samples. As a result of this incomplete sample dissolution, the ICP-MS analysis outcome appeared problematic and inadequate, giving unrepresentative results especially for bauxites. This had a significant impact, mainly on REE values, showing very low REE concentrations in the samples. Tables 10.3a and b show the 4 acids trace and REE results of the BX-N certified reference material samples.

The precipitated residue of both bauxite and red mud waste samples was examined under low vacuum scanning electron microscope (JEOL JSM-5400LV SEM/EDS) in order to find out more details on the kind of the residue and of which elements it is composed. SEM residue pictures from bauxite and red mud waste undissolved samples are shown in Fig. 10.22 to 10.26. SEM/EDS analysis on the bauxite and red mud waste residue showed that it is mainly composed of aluminum and fluorine. It seems that AI was bounded to F, which derived from the hydrofluoric acid (HF) that was added during the digestion process, and created those AIF "crystals" shown in the SEM pictures. Hence, the increased amount of residue found in the bauxite samples compared to the red mud, is due to the high AI bauxite content compared to red mud. Moreover, some zirconium and chromite crystals appeared to be undissolved. Finally, high calcium concentrations in the red mud waste residue are possibly related to some insoluble Ca compounds, which usually appear in red muds as a result of calcination during the Bayer process.

There was an attempt to improve the multi-acid attack method by increasing the hydrofluoric acid (HF) quantity and the digestion time. Ten rather than 4 ml of HF were added and the samples were left to digest for 60 hours (as opposed to 8 hours) with hydrofluoric and perchloric acid (as suggested by Dr. Emma Humphreys-Williams, Natural History Museum, London). Using this method, the dissolution took almost four days and was only applied on BX-N certified reference material samples. The results of this method were much better than the 4 acids method. More specifically, there were much better recoveries of the REE and little residue remained (Table 10.4a and b).

The dissolution of samples was also tested by the sodium peroxide  $(Na_2O_2)$  sintering method. The fusion-sintering process uses sodium peroxide mixed with the sample in zirconia crucibles. The sample is sintered at high

temperature in a furnace and then dissolved in a solution of nitric acid, which results in a solution containing total metals ready for analysis. This method applied again only on the BX-N reference material samples. Although applying this method proved that the REE values were again much better compared to the 4 acids method, some of the other elements showed high blank (Table 10.5a and b). For Zr, this is undoubtedly due to the use of zirconium crucibles. To this point, it is worth mentioning that the literature generally indicates that this method is not really suitable for REE analysis of bauxite samples. This is because bauxite is not totally dissolved and hence not all the amount of REE is dissolved into solution.

To sum up, in terms of REE recovery values, the multi acid CSM dissolution recipe gave the worst results for BX-N bauxite standard, recovering only a very small percent of the original value. The NHM increased HF method resulted in significantly higher REE values, but still below the standard values. On the other hand, the Na<sub>2</sub>O<sub>2</sub> sintering method surprisingly produced higher values compared to the standard. Hence, all of above methods seem to be inappropriate for the complete dissolution and trace element analysis of bauxite and red mud waste samples, and especially if the aim is on the study of REE.

Finally, in accordance with the literature, the lithium borate fusion method was selected as the most appropriate analytical method for the 100% dissolution of bauxite and red mud waste samples. This method usually melts the sample due to the presence of a commercial lithium metaborate (LiBO<sub>2</sub>) or lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) flux, or with a combination of both. For that reason, samples were sent to ACME laboratories in Canada and the LF100 package that analyses reftractory and REE was chosen for the analysis, as it is the most suitable for REE. This was selected to ensure the total dissolution of sample powders, as they were mixed with lithium metaborate/tetraborate and fused, casting into glass discs. Fused discs are entirely homogeneous and eliminate matrix and grain size variability.

# 5.5.2 Dilution with Lithium Borate Fusion Method - Suitability for REE Analysis of Bauxite Samples with ICP-MS

Tables 10.6a, 10.6b, 10.7a and 10.7b show the high accuracy of the  $Li_2B_4O_7$  fusion method used on the BX-N and STD SO-18 (ACME labs standard) certified reference materials. The results of this method for both

bauxite and red mud samples, in comparison with the CSM 4 acid method are shown at Table 10.8 and 10.13 (a, b, c, d and e). Each element recovery percentage was calculated assuming that lithium borate fusion gave the exact value of all elements, given that every sample was dissolved 100%. Finally, duplicate bauxite and red mud waste samples as well as procedural blank samples were run for quality control purposes in all of the aforementioned analytical methods. These results are shown in Tables 10.9, 10.10, 10.11, 10.12 and 10.14 (a and b) and also prove that there was no contamination during the analysis.

The average 4 acids REE recovery from bauxite samples was 27.7%, whereas it surprisingly hit 97.1% on red mud waste samples, making the results almost totally representative. More precisely, this confirms that the more AI the sample has, the harder the dissolution is through the multi-acid attack CSM protocol, making it only useful for red mud waste samples. As far as the bauxite samples are concerned, the very good recovery results of NHM recipe prove that there seems to be a critical point, and if it is achieved to overcome it by adding more HF and increasing the digestion time, it can result almost 100% successful dissolutions and hence reliable data. Results of all 18 red mud waste samples analyzed by 4 acids method and the blank samples ran together are shown at Tables 10.15 and 10.16 (a and b), as only three samples were analyzed using lithium fusions.

#### **5.6 Optical Microscopy**

For the examination of bauxite under the microscope, thin sections, thin polished sections and polished blocks were prepared. For this purpose two samples were selected from each mine (one from each profile) based on the XRD results and colour (yellowish and reddish) in order to represent bauxite's variations as much as possible. These samples were M1 S1, M1 S6, M2 S1, M2 S6, M3 S1, M3 S9, M4 S4 and M4 S6. Additionally, polished blocks were prepared of the ground material.

The idea behind creating thin polished sections was to be able to observe non-metallic minerals and especially clay minerals, while polished blocks from the ground samples were created in order to make it easier to identify REE minerals. Unfortunately, no clay minerals were identified under the optical microscope, possibly because they occur in very low concentrations. Moreover, polished blocks from the ground bauxite material were not helpful for seeing REE minerals, even in the SEM, as these also occur in very low concentrations and their crystals are minute.

Polished blocks were examined at CSM using a Nikon Eclipse E600 Pol microscope (reflected and transmitted) with instant image capture, connected with a Nikon Digital Sight 5MP camera.

# 5.7 Scanning Electron Microscopy (SEM/EDS) and X-Ray Elemental Mapping

Scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometer (EDS) analysis was carried out using a JEOL JSM-5400LV Low Vacuum SEM equipped with an Oxford ISIS EDS system with 20 and 25 kV accelerating voltage at CSM. Elemental mapping was undertaken using the Scanning Microscope in the Laboratory of AUTh (Aristotle University of Thessaloniki, Greece), using a JEOL JSM-840A SEM equipped with an EDS with 20 kV accelerating voltage and 0.4 mA probe current. Backscattered electron images were taken in order to detect areas with different average atomic number.

#### 5.8 Electron Probe Microanalysis (EPMA)

Electron probe microanalysis (EPMA) was carried out by a JEOL JXA-8200 Superprobe with 20 kV accelerating voltage at CSM. Apart from REE and Y, elements such as AI, Fe, Si, Na, Mg and Mn (bauxite's matrix), Ti, Nb and Ta (anatase/rutile crystals), Zr, Sc and Hf (zircon crystals) were calibrated for analysis. In this context, Ca, F, P, CI, Th and U were also calibrated for analysis, in order to find out whether or not these elements occur in REE crystals.

More precisely, Table 5.1 shows the calibration standards. The prefix for the standard could be ignored, as it is unique to the CSM labs. For example, AST-fluorite means that Na was calibrated against fluorite. Table 5.1 also includes the crystals used for the elements, the X-ray lines and the count times. There are two count times, one on the peak and one off peak. In reality there were two off peak measurements one above the peak and one below.

Additionally, Table 5.2 shows the typical detection limits of elements at 3 sigma. Data that were below detection limits or had negative values were removed (Table 10.18). Finally, no generic corrections were applied to the EPMA data. That is because EPMA was used in order to check the stability of REE bearing minerals and then investigate the possibility of analyzing them. Therefore some elements may be overestimated due to overlaps.

Element	X-ray	Crystal	СН	Acc.v	Peak Back		Standard
					Count times		
1	F	Ka	LDE1	20	30	15	Ast-Fluorite
2	Na	Ka	TAPH	20	30	15	Ast-Jadeite
3	Fe	Ka	LIF	20	30	15	Ast-Haematite
4	CI	Ka	PETH	20	30	15	Ast-Tugtupite
5	Si	Ka	TAP	20	20	10	Ast-Jadeite
6	Mg	Ka	TAPH	20	30	15	Ast-Periclase
7	Mn	Ka	LIF	20	30	15	Ast-Bustamite
8	Nb	La	PETH	20	30	15	Ast-M-Nb
9	Al	Ka	TAP	20	30	15	Ast-Jadeite
10	La	La	LIF	20	30	15	Ed-La
11	Ti	Ka	PETH	20	20	10	Ast-Rutile
12	Ce	La	LIF	20	30	15	Ed-Ce
13	Th	Ма	PETH	20	20	10	Ast-M-Th
14	Pr	Lb	LIF	20	40	20	Ed-Pr
15	U	Mb	PETH	20	30	15	Ast-M-U
16	Nd	La	LIF	20	30	15	Ed-Nd
17	Υ	La	PETH	20	30	15	Ed-Y
18	Sm	La	LIF	20	30	15	Ed-Sm
19	Ca	Ka	PETH	20	30	15	Ast-Apatite
20	Eu	La	LIF	20	40	20	Ed-Eu
21	Р	Ka	PETH	20	30	15	Ast-Apatite
22	Gd	La	LIF	20	40	20	Ed-Gd
23	Sc	Ka	PETH	20	30	15	Ast-M-Sc
24	Tb	La	LIF	20	30	15	Ed-Tb
25	Zr	La	PETH	20	20	10	Ast-M-Zr
26	Dy	La	LIF	20	40	20	Ed-Dy
27	Но	Lb	LIF	20	40	20	Ed-Ho
28	Er	La	LIF	20	40	20	Ed-Er
29	Yb	La	LIF	20	40	20	Ed-Yb
30	Та	La	LIF	20	30	15	Ast-M-Ta
31	Hf	La	LIF	20	30	15	Ast-M-Hf

Table 5.1.	EPMA	calibration	standards.
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Element	wt.%	Element	wt.%
Al <sub>2</sub> O <sub>3</sub>	0.12	La <sub>2</sub> O <sub>3</sub>	0.58
FeO	0.13	Ce <sub>2</sub> O <sub>3</sub>	0.40
SiO <sub>2</sub>	0.18	Pr <sub>2</sub> O <sub>3</sub>	0.57
TiO <sub>2</sub>	0.07	Nd <sub>2</sub> O <sub>3</sub>	0.39
CaO	0.03	$Sm_2O_3$	0.31
MnO	0.15	Eu <sub>2</sub> O <sub>3</sub>	0.33
MgO	0.13	$Gd_2O_3$	0.25
Na₂O	0.08	Tb <sub>2</sub> O <sub>3</sub>	0.39
F	0.13	$Dy_2O_3$	0.26
CI	0.02	Ho <sub>2</sub> O <sub>3</sub>	0.39
P <sub>2</sub> O <sub>5</sub>	0.14	Er <sub>2</sub> O <sub>3</sub>	0.24
ZrO <sub>2</sub>	0.30	Yb <sub>2</sub> O <sub>3</sub>	0.26
HfO <sub>2</sub>	0.22	Sc <sub>2</sub> O <sub>3</sub>	0.04
Nb <sub>2</sub> O <sub>5</sub>	0.12	<b>Y</b> <sub>2</sub> <b>O</b> <sub>3</sub>	0.20
Ta <sub>2</sub> O <sub>5</sub>	0.25		
UO <sub>2</sub>	0.08		
ThO <sub>2</sub>	0.10		

Table 5.2. EPMA element detection limit at 3 sigma.

# 5.9 Leaching Methods for Adsorbed REE Cations and the CSM Protocol

Based on various REE leaching methods from the Greek red muds (e.g. Lymperopoulou, 1996; Ochsenkühn-Petropoulou et al., 1996; Ochsenkühn-Petropoulou et al., 2002; Davris et al., 2014; Bourbos et al., 2014; Rao Borra et al., 2015), the aim was to invent and apply successfully a REE leaching protocol for bauxites as well as red muds. Unfortunately, there are no papers in the literature dealing with the leaching of REE in bauxites. Most papers refer to the leaching of clay minerals, red mud waste or ion-absorption deposits. Bauxite has a different chemistry compared to the aforementioned cases. The main difference is that it has significantly lower amounts of Si compared to clays and ion-absorption deposits, while it has significantly higher amounts of Al compared to red mud. Moreover, REE appear to be readily leachable from red mud waste by diluted mineral acids, whereas these elements cannot be leached from bauxite under the same experimental conditions (Fulford et al., 1991). Hence, there are concerns about applying the aforementioned techniques straight to bauxite ore. Among the most interesting REE leaching protocols are the following:

A) Extraction process used at mines in China for ion-absorption deposits: The Chinese extraction of REE adsorbed onto clay minerals is generally based on leaching by electrolyte solutions such as  $(NH_4)_2SO_4$  and  $NH_4Cl$  to make a rare earth leach liquor (He et al., 1983; Gupta and Krishnamurthy, 2002; Tian et al., 2010, 2011, 2013), which is then precipitated to make a mixed REE compound (e.g. oxalate) that is shipped to the processing plant. Various potentially improved methods have been proposed in the last few years, including precipitation and non-precipitation processes that main REE in solution along with solvent extraction, ion exchange or liquid membrane methods. The leaching reaction of the rare earth ore with ammonium sulfate has an equation as follows (Chi and Tian, 2008):

$$\{AI_{4}[Si_{4}O_{10}](OH)_{8}\}^{-}_{m} \cdot nRE^{3+}_{(s)} + 3nNH_{4}^{+}_{(aq)} \rightarrow \{AI_{4}[Si_{4}O_{10}](OH)_{8}\}^{-}_{m}x3nNH_{4}^{+}_{(s)} + nRE^{3+}_{(aq)} + nRE^{3+}_{(aq)$$

Where (s) is solid phase and (aq) is the aqueous phase.

The leaching is normally carried out under neutral or slightly acidic conditions (Bao and Zhao, 2008). It is done either in tanks or by in situ leaching. There is some query as to whether the acidic pH also dissolves soluble REE minerals such as REE fluorcarbonates.

2) BCR (European Community Bureau of Reference) sequential extraction procedure: This is a well-known and accepted method used to establish the residence of trace elements in soils and sediments. The samples are treated with a series of reagents selected for their ability to react with different, major, components of the matrix and release associated trace metals. For years, various scientists used and proposed different protocols. Tessier et al. (1979) is the best-known early paper (Table 5.3). However, in the 1990s the evolution of these protocols was used to propose a standard BCR European method for a three-step sequential extraction protocol (Ure et al., 1993 and Table 5.3). Following inter laboratory tests, this protocol was updated (Rauret et al., 1999, 2000) and it seems to be this method that is now most commonly used (Table 5.3).

All of these variations based on the BCR method have the problem that they have a first step that removes both exchangeable cations and soluble

carbonates. But it is important for a REE leaching protocol to be able to differentiate these two components, as it is an important point in the Chinese samples because they contain rare earth rich fluorcarbonate minerals. Sanematsu et al. (2013) used a method based on the BCR method of Rauret et al. (1999, 2000) for ion adsorption clays in Thailand. However, they substituted the first step using ammonium sulphate, which is also used for cation exchange at many of the mines in China for the first step in BCR method (Table 5.3). The first step was carried out at a slightly acidic pH that may also dissolve some of the carbonate.

It would be most instructive to use an exchange mechanism at neutral pH in order to have the best test of exchangeable components versus soluble components. The paper that originally established the method of stepwise leaching by Tessier et al. (1979) has an additional first step for exchangeable cations using magnesium chloride or sodium acetate at pH 7 and then a second step to remove carbonates with sodium acetate at pH 5 (obtained with acetic acid). Consequently, the new "CSM" protocol suggests adding (just) the magnesium chloride step to the front of the Rauret et al. (1999) BCR method. The disadvantage with this is that it adds an extra step to the procedure and will make the stepwise leaching process even lengthier, but it would give the most rigorous test. There is a slight advantage in using ammonium sulphate in the first step because it is the most widely used exchange agent on mine sites in China, but magnesium chloride is also mentioned in some reports.

A faster method was proposed by Moldoveanu and Papangelakis (2013) in a report of tests on material from the Tantalus ion adsorption clay deposit in Madagascar. They used 0.5 M ammonium sulphate, similar to Sanamatsu et al. (2013) for the cation exchange step (and also tested sodium chloride and seawater), but did no further stepwise leaching. It would be possible to use the first step of Sanematsu et al. (2013), or the first step of Tessier et al. (1979) on its own to check for exchangeable cations, and then continue on a smaller number of samples to determine the other residency of REE.

The final step in the procedures in Table 5.3 is to analyze the insoluble residue. This is best done by the same method as whole rock analysis, so that all the material is dissolved and then the results of stepwise leaching and whole rock analysis can be compared. To make a mass balance comparison, the weights of residue at each stage would need to be recorded and then compared

#### with a whole rock analysis to check that all components are accounted for.

Fra	lection	Nominal target phase(s)	Protocol A (Tessier et al., 1979)	Protocol B (original BCR) (Ure et al., 1993)	Protocol C (revised BCR) (Rauret et al., 1999, 2000)	Protocol D (Sanematsu et al., 2013)	Proposed protocol: Mixture of Tessier et al. (1979) and Rauret et al. (1999)
Sa	mple used		1 g sample used		1 g sample	1 g powdered	1 g sample
)	Exchangeable		1 h with 8 mL of either (1 M MgCl <sub>2</sub> , pH 7.0) or sodium acetate solution (1 M NaO Ac, pH 8.2), continuous agitation			40-ml of 0.5 M ammonium sulfate (adjusted at $pH=4$ with $H_2SO_4$ )	1 h with 8 mL (1 M MgCl, pH <i>7.0)</i>
2)	Exchangeable, water and acid soluble	Soluble species, carbonates and cation exchange sites	8 mL of 1 M NaO Ac adjusted to pH 5.0 with acetic acid (HO Ac), continuous agitation	0.11 mol I <sup>-1</sup> acetic acid	0.11 mol I <sup>-1</sup> acetic acid		0.11 mol I <sup>-1</sup> acetic acid
3)	Reducible	Iron and manganese oxyhydroxid es	20 mL of either 0.3 M Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> + 0.175 M Na-citrate + 0.025 M H- citrate (Anderson and Jenne, 1970) or 0.04 M NH <sub>2</sub> OHHCl in 25% (v/v) HO Ac at 96 $\pm$ 3 °C, occasional agitation	0.1 mol I <sup><sup>-1</sup> hydroxylammoni um chloride at pH 2</sup>	40 ml 0.5 mol l <sup>−1</sup> hydroxylammonium chloride at pH 1.5	40 ml of 0.5 M hydroxylammonium chloride (adjusted to pH=2 with HNO <sub>3</sub> )	0.5 mol I <sup>-1</sup> hydroxylammonium chloride at pH 1.5
1)	Oxidisable	Organic matter and sulphides	3 mL of 0.02 M HNO <sub>3</sub> and 5 mL of 30% $H_2O_2$ adjusted to pH 2 with HNO <sub>3</sub> at 85 ± 2 °C, 2h occasional agitation. Additional 3 mL of 30% $H_2O_2$ (pH 2 with HNO <sub>3</sub> ) at 85 ± 2 °C for 3h. 5 mL of 3.2 M NH <sub>4</sub> O Ac in 20% (v/v) HNO <sub>3</sub> . Sample diluted to 20 mL and agitated for 30 min (Gupta and Chen, 1975)	Hydrogen peroxide followed by 1.0 mol I <sup>-1</sup> ammonium acetate at pH 2	20 ml 8.8 M hydrogen peroxide followed by 1.0 mol I <sup>-1</sup> ammonium acetate at pH 2	20 ml of 8.8 M hydrogen peroxide	Hydrogen peroxide followed by 1.0 mol I <sup>-1</sup> ammonium acetate at pH 2
5)	Residual		HF-HCIO₄	Aqua regia (or HF/HNO <sub>3</sub> )	Aqua regia	No residual determination	Our standard whole rock procedure – either multiple acid or sodium peroxide sinter

#### Table 5.3. Comparison of stepwise leaching methods.

1

Note: Prof. Wall established the CSM Stepwise REE Leaching Protocol on 15/04/2014 using material supplied by Mr. Mouchos and Dr. Van Veen (Camborne School of Mines), Dr. Palumbo-Roe (British Geological Survey) and Mr. Thompson (Camborne School of Mines / Imerys Minerals Ltd.).

There are standards available for the BCR method but none for the BCR or any other stepwise leaching method have REE. Therefore a standard BCR transition metal standard will probably have to be used for quality control. The BCR-701 certified reference material is lake sediment and has been certified for Cd, Cr, Cu, Ni, Pb and Zn supplied by Institute for Reference Materials and Measurements from the European Commission (IRMM) (Sutherland, 2010).

# 6. Results

### 6.1 Introduction

This chapter presents and discusses the XRD major mineralogy results of all bauxite samples analyzed. It also identifies the whole rock compositions of bauxite and red mud waste samples by XRF and ICP-MS analysis. The focus is on the lithium borate fusions method results that are the most accurate, which is followed by the discussion of these results for both bauxite and red mud waste and their correlations.

In this chapter, apart from the major mineralogy of bauxite there are also presented its secondary minerals, with particular focus on the REE bearing minerals. The study was undertaken using an optical microscope, scanning electron microscope (SEM) and electron probe microanalyzer (EPMA). The last method provides the chemical composition of the REE bearing minerals and hence adds significantly to their identification.

This chapter also reviews published REE leaching test methods from the Greek red mud waste. Additionally, it assesses the feasibility of applying other leaching protocols to bauxite and red mud waste. Finally, it presents the results from applying a protocol suggested by Sanematsu et al. (2013) to various REE rich samples, including the Greek bauxite and red mud waste samples.

# 6.2 Mineralogy and Geochemistry of Bauxite

# 6.2.1 XRD Results and Major Mineralogy of Bauxite

XRD interpretations showed that bauxite samples are composed of the AI minerals diaspore and boehmite, the Fe minerals, hematite and goethite, the Ti mineral anatase, and the clay mineral kaolinite (Fig. 6.2 to 6.5 and Table 6.1). Diaspore appears in all samples and is the predominant mineral where boehmite does not exist or is in small concentrations. However, in samples where boehmite is the predominant mineral, diaspore is absent or found in smaller concentrations. The exception is sample M4 S10 where boehmite and diaspore occur in almost equal concentrations. Hematite occurs in various concentrations in all samples apart from M2 S1. Unlike hematite, goethite does

not appear in all samples and always occurs in low concentrations. Anatase also appears in every sample but in very low concentrations as well.

Finally, kaolinite appears in very low concentrations only in two samples (M1 S1 and M1 S5) of Mine 1, both of which come from the hanging wall of the mine at the two different profiles sampled. It is worth mentioning that kaolinite may occur in other samples too, but it is hard to decide if these weak peaks are noise and below the detection limit of approximately 5% or indicate the presence of the specific mineral. Additionally, the XRD software didn't perfectly match these peaks to the patterns of kaolinite. Hence, there is always the possibility for these peaks to refer to another as yet unidentified mineral.

The color of the powders appears to be a reasonably reliable indicator of the iron content of the sample (Fig. 6.1 and Table 6.1). Bauxite can be distinguished in four colors, which are red or reddish brown (hematite rich), yellow (goethite rich), gray (small iron content) and white (iron depleted). The bauxite in this study ranges from yellow to brown and red. The comparison of the sample color with its XRD pattern denotes the iron content. The darker the color, the higher is the iron content of the sample.



Figure 6.1. Powdered bauxite sample colors. From left to right are samples from Mine 1 to Mine 4.



Figure 6.2. XRD patterns for samples from Mine 1 (Vargiani).  $1^{st}$  and  $2^{nd}$  profiles are shown at the upper and lower picture respectively. D= Diaspore, B= Boehmite, H= Hematite, G= Goethite, A= Anatase and K= kaolinite. Black spectrum represents the hanging wall sample, while the green one shows the footwall sample respectively.



Figure 6.3. XRD patterns for samples from Mine 2 (Silas).  $1^{st}$  and  $2^{nd}$  profiles are shown at the upper and lower picture respectively. D= Diaspore, B= Boehmite, H= Hematite, G= Goethite and A= Anatase. Black spectrum represents the hanging wall sample, while the purple one shows the footwall sample respectively.



Figure 6.4. XRD patterns for samples from Mine 3 (Gouves).  $1^{st}$  and  $2^{nd}$  profiles are shown at the upper and lower picture respectively. D= Diaspore, B= Boehmite, H= Hematite, G= Goethite and A= Anatase. Black spectrum represents the hanging wall sample, while the purple ( $1^{st}$  profile) and green ( $2^{st}$  profile) spectra show the footwall sample respectively.



Figure 6.5. XRD patterns for samples from Mine 4 (Spartolakka).  $1^{st}$  and  $2^{nd}$  profiles are shown at the upper and lower picture respectively. D= Diaspore, B= Boehmite, H= Hematite, G= Goethite and A= Anatase. Black spectrum represents the hanging wall sample, while the purple one shows the footwall sample respectively.

Table 6.	1. Major	mineralogy	of	bauxite	samples,	as	determined	by	XRD	(M=
minerals	in high a	mounts and	X=	= minera	ls in low a	mοι	unts respecti	vely	/).	

Sample	Altitude	Color	Boehmite	Diaspore	Hematite	Goethite	Anatase	Kaolinite		
	Mine 1 (Vargiani) Profile 1									
M1 S1	577.1 m	Ochre	М	Х	Х	Х	Х	Х		
M1 S2	575.5 m	Brown-Red	М	Х	М		Х			
M1 S3	574 m	Red		М	М		Х			
M1 S3 Dupl	574 m	Red		М	М		Х			
M1 S4	572.5 m	Brown-Red		М	М		Х			
Mine 1 (Vargiani) Profile 2										
M1 S5	571.5 m	Light Brown		М	Х	Х	Х	Х		
M1 S6	570 m	Brown		М	М	Х	Х			
M1 S6 Dupl	570 m	Brown		М	М	Х	Х			
M1 S7	568 m	Brown		М	М		Х			
M1 S8	566 m	Brown		М	М		Х			
	-		Mine 2 (S	Silas) Profile	e 1					
M2 S1	516 m	Yellow		M		Х	Х			
M2 S2	514 m	Brown		M	М		Х			
M2 S3	512 m	Light Brown		М	Х	Х	Х			
M2 S3 Dupl	512 m	Light Brown		M	Х	Х	Х			
M2 S4	510 m	Brown		М	М	Х	Х			
M2 S5	508.5 m	Dark Brown	Х	М	М		Х			
	-		Mine 2 (S	Silas) Profile	2					
M2 S6	500 m	Brown	Х	M	M	Х	Х			
M2 S7	497.5 m	Brown		M	M		X			
M2 S8	495 m	Ochre		M	X	Х	X			
M2 S8 Dupl	495 m	Ochre		M	X	Х	X			
M2 S9	492.5 m	Light Brown		M	X	Х	Х			
M2 S10	490.5 m	Brown		M	М		Х			
	T		Mine 3 (Go	ouves) Profi	le 1			r		
M3 S1	307.3 m	Ochre		M	X	X	X			
M3 S2	305.5 m	Dark Brown		M	M		X			
M3 S3	304 m	Dark Brown		M	M		X			
NI3 54	302.5 m	Dark Brown	IVI	X	IVI		X			
M2 S5	302.5 m	Dark Brown			IVI	V				
1013 33	301 11	Dark Brown	Mino 3 (Gr			^	^	l		
M2 S6	200.2 m	Light Brown				×	V			
M3 S7	207.5 m	Dork Brown		N	^ 					
M3 57 M3 58	306 m	Dark Brown	X	M	M	~	X			
M3 S9	304.5 m	Dark Brown	M	X	M		X			
M3 S9 Dupl	304.5 m	Dark Brown	M	X	M		X			
	001.0111	Ban Brown	Mine 4 (Spai	rtolakka) Pr	ofile 1		~			
M4 S1	236.2 m	Red		M	M	Х	Х			
M4 S1 Dupl	236.2 m	Red		M	M	X	X			
M4 S2	234.5 m	Red		М	М	Х	Х			
M4 S3	233 m	Red		М	М	Х	Х			
M4 S4	231.5 m	Brown-Red		М	М		Х			
M4 S5	230 m	Brown	М	Х	М		Х			
			Mine 4 (Spai	rtolakka) Pr	ofile 2					
M4 S6	245.5 m	Brown		М	М	Х	Х			
M4 S7	244 m	Brown-Red		М	М	Х	Х			
M4 S8	242.5 m	Brown		М	Х	Х	Х			
M4 S9	241 m	Brown		М	Х		X			
M4 S10	239.5 m	Brown-Red	M	М	Μ		Х			
M4 S10 Dupl	239.5 m	Brown-Red	М	М	М		Х			

More precisely, yellow and light brown samples usually have low hematite and goethite content such as M2 S1 sample that has the lightest color because it has the lowest iron oxide content (absence of hematite and small amount of goethite). On the other hand, the brown or red samples show high hematite peaks (iron content). Finally, it is worth mentioning that in the first three mines the hanging wall samples are light colored with low or very low iron content (apart from M2 S6 sample). Moreover, kaolinite occurs only in both hanging wall samples of Mine 1. Finally, all Mine 4 samples are dark colored, indicating that "Spartolakka" mine has the highest iron content and it is rather homogeneous in terms of its mineralogy and chemistry, compared to the other three mines.

In terms of the spectra interpretations, boehmite gives its highest peaks at 14.5°, 28°, 38.5° and 49°. Diaspore highest peaks are at 22°, 39°, 42.5°, 43.5° and 56.5°. Hematite's highest peaks are at 33.5°, 36° and 54°. As far as the low concentration minerals are concerned, goethite's clearest peak is at 21°, 25.5° for anatase and 12.5° for kaolinite. These peaks appear cleaner at the beginning of the patterns because the noise level is very low and can be easily observed and also because there are no higher peaks of other high concentration minerals close to overlap. These two reasons are particularly helpful for kaolinite detection, as its concentration is very close to the detection limits.

Furthermore, at the end of the patterns (> 50) many peaks of boehmite, diaspore and hematite occur. This sometimes causes peaks to overlap or two or more peaks to result to one bigger peak. The big peak at 49° is an example where boehmite and hematite peaks are equally strong and may result one big peak at samples where the two different peaks are not clear.

All duplicate samples have the same mineralogy and color in comparison with the original samples although there were slight variations, especially in peak height (Fig. 10.13 to 10.20).

Finally, the main mineralogy of bauxite as it is identified from XRD analysis is generally in line with the literature on the Parnassus-Giona bauxite (Spoudeas, 1997; Tsirambides, 2005; Tsirambides and Filippidis, 2012). The main minerals identified are diaspore, boehmite, haematite, anatase/rutile and kaolinite but quartz and calcite that usually occur as well are absent from this study's samples or were below the detection limits of XRD.

# 6.2.2 XRF Analysis for Bauxite Samples

The Delphi-Distomon S.A. extracted bauxite ore chemical compositions for the 2012 and 2011 years are shown at Tables 10.1a and b. Comparing the semi-quantitative results analyzed at CSM laboratories to the quantitative results provided by the company, there is as expected a slight decrease of all values and totals in the semi-quantitative analysis (Table 10.2). This is possibly because the results are semi-quantitative.

The iron content seems to be the most problematic as the M2 S1 sample for instance appears to have 18.7% Fe, while the same sample in the XRD analysis appears to have very low iron content (which is assumed by the absence of hematite peaks and the very low goethite peaks) and also its color is yellowish. Undoubtedly, bauxite is an heterogeneous ore and different grains of the same sample were analyzed at XRD and XRF, but on the other hand, so big variation in the iron content indicates that Fe in the XRF might not be calibrated very well.

Generally, major elements show typical bauxite concentrations mainly composed of AI and Fe oxides, and lower amounts of Ti, Si, Ca and S oxides. Silica is the most variable element, with its concentrations being very high in specific locations (e.g. M3 S9 Dupl. at Table 10.2). The LOI values are about 12%.

Mn, Mg, Na, P and K are minor elements in very low concentrations, whereas Cr, Ni and V are characteristic trace elements that can be found in relatively high concentrations that are usually much more than 500 ppm and occasionally can reach about 2000 ppm. Additionally, the presence of Zr and Nb in Greek bauxites is very important, as both elements can be found in all samples (Zr at about 500 ppm and Nb at 50 ppm respectively). There was also an indication of relatively high Ce in M2 S7 and M4 S9 samples.

#### 6.2.3 Trace Elements and REE Results of Bauxite Samples

In order to get a clear and accurate picture of the trace and rare earth element contents in all bauxite samples, there their average concentrations (including the duplicate samples either from sampling or the ICP-MS duplicates) were calculated. Only data produced by lithium metaborate fusion and ICP-MS were used in this section.

In more detail, among other elements (such as Cr and Ni), V and Zr are found in high concentrations in bauxites, as it is already shown in the XRF results (Fig. 6.6). V appears to have important variations between samples ranging between 250 and 1186 ppm, whereas Zr seems to have a standard presence ranging between 421 and 584 ppm (Table 6.2a). Co, Ga and Nb also appear to be in standard concentrations in every bauxite samples (about 50 ppm). Finally, Th, U, Ta and Hf occur in very low but steady concentrations. V tends to increase with Co, Zr increases with Hf, Th is increasing with U and Nb with Ta. W is high due to bauxite sample preparation contamination.



Figure 6.6. Pie charts showing the average trace element (left) and REE (right) concentrations of the B3 horizon.

Ga concentration in Mediterranean bauxites ranges from 5 to 812 ppm with an average of 53 ppm (Schulte and Foley, 2014). Ga in this study's bauxite samples ranges from 47.9 to 63.5 ppm, hence its average value is 56.6 ppm that is very close to the literature. Gamaletsos et al. (2011) recently proved that Ti-phases of the Parnasos-Giona bauxites, and particularly anatase, host significant amounts of Th. This conclusion indicated an average of 73 ppm Th in anatase grains together with abundant Nb (3,356 ppm), Ta (247 ppm) and U (33 ppm). More precisely, LA-ICP-MS results on anatase crystals show that Th concentration varies in the range of 13–117 ppm, together with abundant Nb (947–11,865 ppm), Ta (55–982 ppm) and U (6–97 ppm). Figure 6.7 graphs the Th–U and Nb–Ta correlation.



Figure 6.7. Relation between V and Co (upper left), Zr and Hf (upper right), Th and U (lower left) and Nb and Ta (lower right) in B3 bauxite samples.

As far as the REE in bauxite are concerned, SREE varies between 126.8 and 679.8 ppm with the average concentration being 327.8 ppm. SREE+Y ranges between 158.7 and 716.5 ppm (average is 369.2 ppm) (Table 6.2b). The middle sample of the 1<sup>st</sup> profile of Mine 1 (M1 S3 Avg) has the lowest  $\Sigma REE$  and  $\Sigma$ LREE concentrations (including the lowest Ce value, which is 86.2 ppm), while the top sample of the 1<sup>st</sup> profile of Mine 3 (M3 S1) has the highest  $\Sigma REE$  and ΣLREE concentrations. Even if the close to the bottom sample of the 1<sup>st</sup> profile of Mine 3 (M3 S4 Avg) has the highest values in most of the REE's and the highest  $\Sigma$ HREE content, the top sample of the 1<sup>st</sup> profile of Mine 3 (M3 S1) has the highest Ce value (598.2 ppm), making it the highest  $\Sigma REE / \Sigma LREE$  sample, given that Ce is the predominant REE. Furthermore, the bottom sample of the 1<sup>st</sup> profile of Mine 2 (M2 S5) has the highest La and Pr values. La (159 ppm) is almost as high as Ce (178.9 ppm) in this sample. The middle sample of the 1<sup>st</sup> profile of Mine 4 (M4 S3) has the lowest SHREE concentrations. Average  $\Sigma LREE / \Sigma HREE$  ratio is 9.9, the highest ratio appears in the top sample of the 1<sup>st</sup> profile of Mine 3 (M3 S1), whereas the lowest is in the close to the bottom sample of the 1<sup>st</sup> profile of Mine 3 (M3 S4 Avg).



Figure 6.8. Average REE concentrations in the eight bauxite profiles sampled. Mine 1 to 4 (upper to lower) and profiles 1 (left) and 2 (right).

Ce generally comprises more than 50% of the total REE, followed by La and Nd. Y does also occur in relatively high concentrations, but much lower than Ce of course (Fig. 6.8). Moreover, Ce appears to be the predominant element in all bauxite profiles. Mine 3 has the lowest Ce and La, Y and Nd content (Fig. 6.9). It is worth mentioning that elements such as Co, V, Th and U tend to increase with REE, as they appear in high concentrations in REE rich samples (Fig 6.10). Finally, Ce as the predominant rare earth element generally increases with LREE contents but this does not clearly happen with the HREE (Fig 6.11). On the other hand, the correlation between  $\Sigma$ HREE and  $\Sigma$ LREE is clearer (Fig. 6.11).



Figure 6.9. Average REE concentration percentages in the four bauxite mines of the B3 horizon. Upper left and right are Mines 1 and 2, whereas down left and right are Mines 3 and 4.

Sample Name Ва Ве Со Cs Ga Hf Nb Rb Sn Sr Та Th U V W Zr 111.0 2.0 60.4 0.3 48.1 13.7 51.8 4.6 51.6 6.2 469.0 147.4 513.7 M1 S1 1.4 11.0 240.2 M1 S2 40.0 1.0 19.6 0.1 50.6 14.6 52.2 0.2 11.0 25.2 4.2 60.7 5.0 347.0 112.6 500.8 M1 S3 Avg 37.5 4.0 24.3 0.1 48.8 0.7 11.0 21.5 3.9 47.4 5.1 347.0 478.3 59.1 13.5 64.7 M1 S4 23.0 4.0 14.3 0.1 53.2 14.7 51.3 12.0 27.2 3.7 53.8 5.2 373.0 518.6 0.1 61.6 M1 S5 185.0 3.0 27.6 0.1 54.1 14.7 53.7 0.7 13.0 26.8 5.0 57.2 6.3 250.0 126.7 526.9 M1 S6 Avg 111.0 3.5 45.6 0.2 55.5 14.4 0.7 11.5 23.9 4.6 53.6 5.2 334.5 110.9 507.0 50.6 M1 S7 84.0 2.0 31.8 0.4 55.8 14.6 52.8 0.9 12.0 21.6 4.1 54.5 5.7 433.0 98.5 537.3 M1 S8 53.0 4.0 30.0 0.1 54.2 14.8 53.7 0.1 12.0 20.9 4.5 55.5 5.8 410.0 118.7 520.0 M2 S1 2.0 90.9 0.1 15.4 56.1 0.2 13.0 52.2 4.4 53.7 747.0 81.5 541.5 42.0 56.6 10.1 M2 S2 85.0 2.0 41.3 0.1 55.5 57.3 0.6 12.0 42.7 5.2 54.3 9.2 630.0 125.6 584.2 16.7 M2 S3 Avg 2.0 25.6 0.1 31.5 42.0 7.3 509.5 93.5 55.2 14.2 57.3 0.2 12.0 4.6 593.0 163.2 M2 S4 2.0 53.8 44.5 4.4 46.1 7.6 490.1 88.0 43.3 0.1 63.5 13.5 0.1 11.0 562.0 103.2 M2 S5 86.0 4.0 54.2 1.0 55.3 13.4 49.3 5.0 11.0 48.1 5.3 47.1 7.6 826.0 176.5 492.6 M2 S6 85.0 5.0 41.5 0.1 47.9 15.7 60.8 0.1 14.0 25.0 5.1 66.5 10.5 705.0 147.5 573.0 M2 S7 67.0 5.0 33.9 0.1 60.7 13.7 49.2 0.1 11.0 22.2 4.3 50.9 172.5 491.9 8.8 466.0 0.2 M2 S8 Avg 28.0 5.0 31.4 0.2 57.5 12.1 48.1 11.0 25.3 3.9 46.4 8.2 642.0 132.1 456.7 38.4 3.9 M2 S9 39.0 5.0 0.1 54.1 12.2 47.3 0.1 11.0 20.2 51.0 9.4 707.0 164.3 427.2 M2 S10 40.0 4.0 39.9 0.1 55.5 13.8 48.4 0.1 12.0 22.8 4.4 53.3 9.6 724.0 168.0 505.0 M3 S1 64.0 2.0 100.5 0.4 54.5 14.1 51.3 0.9 13.0 38.6 4.7 57.8 8.7 1021.0 120.8 495.4 M3 S2 51.0 4.0 32.1 0.1 57.3 14.5 54.9 0.1 13.0 45.4 4.0 56.8 11.5 1112.0 75.5 546.2 M3 S3 65.0 8.0 47.9 0.2 62.7 14.8 52.6 0.4 12.0 33.5 4.6 52.6 14.2 1186.0 113.2 518.4 M3 S4 Avg 60.5 7.0 150.8 1.1 53.1 13.8 50.4 3.4 11.5 43.4 4.4 47.1 11.3 800.0 56.5 500.7 M3 S5 95.0 6.0 76.4 0.4 57.8 14.0 49.2 0.8 14.0 41.7 4.2 52.6 12.0 933.0 133.2 497.5 M3 S6 72.0 6.0 71.9 0.5 57.8 13.4 50.7 2.5 12.0 67.3 4.4 60.9 11.5 897.0 61.9 487.4 M3 S7 34.0 4.0 13.5 0.1 63.5 13.8 50.7 0.1 11.0 64.8 4.0 59.3 10.1 1015.0 50.4 508.4 M3 S8 182.0 6.0 75.4 3.4 52.1 11.7 41.4 13.0 10.0 80.2 3.7 56.5 7.7 996.0 83.5 421.0 M3 S9 Avg 3.1 42.2 12.0 3.5 422.9 164.0 5.5 51.6 12.1 10.0 68.3 53.8 8.2 803.5 54.9 46.8 3.0 0.4 45.9 4.2 119.2 446.2 M4 S1 Avg 58.5 40.8 61.5 12.9 10.0 33.1 43.7 6.0 439.0 1.1 M4 S2 Avg 45.4 3.9 41.5 5.5 25.8 0.3 62.2 12.5 0.8 10.5 27.0 41.8 5.9 419.5 84.2 443.1 M4 S3 3.8 45.2 5.2 51.0 4.0 20.6 0.1 54.7 12.6 46.1 0.1 11.0 22.8 408.0 81.7 454.4 M4 S4 29.0 4.0 20.2 0.1 61.1 13.7 51.9 0.2 11.0 38.5 3.9 50.4 6.0 531.0 74.0 491.5 M4 S5 71.0 6.0 45.4 1.5 58.7 13.3 46.7 5.4 11.0 50.8 3.7 47.9 6.8 492.0 49.3 485.8 M4 S6 52.0 2.0 18.6 0.2 57.5 12.5 47.4 0.2 10.0 22.2 4.1 48.4 5.2 408.0 88.7 460.7 M4 S7 58.0 1.0 24.2 0.1 57.3 13.5 48.8 0.2 11.0 26.0 4.3 54.1 5.1 590.0 120.6 495.6 M4 S8 2.0 52.3 83.0 21.6 0.2 59.5 13.1 49.3 0.3 11.0 32.3 4.1 6.0 670.0 95.1 499.0 M4 S9 31.0 3.0 47.2 0.1 62.4 14.6 54.2 0.1 12.0 33.7 4.1 47.7 6.5 585.0 74.0 518.4 M4 S10 Avg 45.5 3.0 61.7 0.4 5.0 49.0 57.7 15.8 55.8 0.6 12.0 39.7 7.2 543.0 116.5 558.1 70.4 3.8 44.2 0.4 56.6 13.8 50.7 1.4 11.6 41.9 4.3 52.0 7.8 632.8 106.2 498.0 Average

Table 6.2a. Trace element values (ppm) of all bauxite samples prepared using the lithium borate fusion – dissolution procedure. Blue values indicate each element's highest value and values in red are each element's lowest value respectively.

Note: Samples with Avg indication represent the average element values of the original sample and its duplicates (sampling or/and ICP-

MS duplicates).

Sample Name Altitude (m) La Ce ΣREE ΣREE+Y ΣLREE ΣHREE ΣHREE+Y L/H La/Y La/Lu Ce/Ce\* Eu/Eu\* Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Υ Mine 1 (Vargiani) Profile 1 M1 S1 577.1 404.2 13.0 55.8 13.9 3.0 12.9 26.7 1.8 9.7 1.9 5.0 0.8 5.2 0.7 44.6 554.5 599.1 513.6 40.9 85.5 12.6 0.6 36.1 5.2 0.7 M1 S2 575.5 9.6 120.9 2.4 7.9 2.0 0.5 3.2 0.7 1.1 4.1 0.7 162.4 193.2 142.8 19.6 7.3 0.3 14.5 6.1 5.1 3.7 0.6 30.8 50.4 0.6 M1 S3 Ava 2.2 4.7 1.1 4.3 32.0 5.9 15.6 574 10.5 86.2 7.7 1.7 0.4 2.6 0.6 3.7 0.6 0.7 1267 158.7 108.3 18.5 50.4 0.3 4.4 0.6 M1 S4 572.5 18.9 96.2 3.5 11.6 2.2 0.6 3.2 0.7 5.8 1.4 4.6 0.8 5.3 0.9 37.8 155.5 193.3 132.3 23.1 60.9 5.7 0.5 22.0 2.9 0.6 Mine 1 (Vargiani) Profile 2 M1 S5 571.5 253.2 10.6 171.8 2.7 10.5 2.2 0.6 3.7 0.7 5.4 1.3 34.6 218.6 197.8 20.7 55.3 9.6 0.3 16.3 7.8 0.6 3.8 0.6 4.1 0.7 M1 S6 Ava 570 8.3 181.2 2.2 8.3 2.1 0.5 3.4 0.7 5.0 1.1 3.5 0.6 3.8 0.6 33.1 221.2 254.3 202.0 19.2 52.3 10.5 0.2 13.4 10.2 0.6 M1 S7 568 28.2 273.9 7.1 25.5 5.2 6.4 5.5 44.3 414.2 339.9 11.3 0.6 32.8 4.7 0.6 1.2 1.1 7.3 1.6 5.1 0.8 0.9 369.9 30.0 74.3 M1 S8 566 21.9 348.8 4.7 17.0 3.4 0.8 5.4 0.9 6.7 1.6 5.1 0.8 5.7 0.9 43.0 423.7 466.7 395.8 27.9 70.9 14.2 0.5 25.5 8.3 0.6 Mine 2 (Silas) Profile 1 M2 S1 516 16.2 140.0 3.4 13.4 3.0 0.7 4.2 0.9 6.4 1.4 4.3 0.6 4.4 0.7 40.7 199.5 240.2 175.9 23.6 64.3 7.5 0.4 23.1 4.6 0.6 M2 S2 514 3.4 16.9 194.8 12.2 2.9 0.6 4.0 0.8 5.6 1.2 4.0 251.8 286.2 230.2 21.6 56.0 10.7 0.5 25.2 6.2 0.6 0.6 4.1 0.7 34.4 M2 S3 Avg 512 11.9 193.0 3.2 12.3 3.2 0.8 4.5 0.9 6.1 1.4 4.2 0.6 4.5 0.7 37.4 247.2 284.6 223.6 23.7 61.0 9.5 0.3 16.8 7.5 0.6 M2 S4 510 15.5 186.7 5.9 22.5 5.2 1.2 5.4 1.0 6.8 1.4 4.4 0.7 5.1 0.8 36.9 262.6 299.5 235.8 26.8 63.7 8.8 0.4 20.1 4.7 0.7 M2 S5 159.0 178.7 20.6 56.1 9.9 2.2 9.5 1.7 10.6 2.1 5.9 1.0 6.8 45.4 465.1 510.5 424.3 40.8 10.4 3.5 145.9 0.8 0.7 508.5 1.1 86.2 Mine 2 (Silas) Profile 2 M2 S6 500 384.8 58.8 11.7 40.7 8.0 1.7 9.5 1.4 9.2 1.9 5.4 0.9 5.8 0.9 53.2 540.6 593.8 504.0 36.6 89.8 13.8 1.1 68.4 3.6 0.6 M2 S7 497.5 28.3 467.6 6.7 24.2 5.2 1.2 7.0 1.0 6.8 1.4 4.5 0.7 4.9 0.8 39.5 560.3 599.8 532.0 28.3 67.8 18.8 0.7 37.2 8.2 0.6 M2 S8 Avg 37.5 3.2 495 9.1 33.5 7.0 1.6 7.9 1.2 8.2 1.7 5.0 5.6 45.1 413.1 335.1 33.0 78.0 10.2 0.8 0.6 248.1 0.8 0.9 368.0 42.6 M2 S9 6.8 23.8 5.6 276.4 318.5 247.3 29.1 8.5 0.7 32.2 3.2 0.7 492.5 28.3 183.2 5.3 1.2 5.9 1.1 7.1 1.5 4.9 0.8 0.9 42.1 71.2 M2 S10 490.5 39.2 282.6 10.0 35.3 8.5 1.8 7.9 1.5 9.7 2.0 6.1 1.1 7.8 1.1 52.6 414.6 467.2 375.5 39.1 91.7 9.6 0.7 34.4 3.5 0.7 Mine 3 (Gouves) Profile 2 M3 S6 309.2 24.1 149.8 5.0 16.9 3.4 0.8 4.3 0.8 5.9 1.3 4.1 0.7 4.8 0.7 36.8 222.7 259.5 199.3 23.4 60.2 8.5 0.7 33.0 3.3 0.6 65.2 M3 S7 307.5 36.5 192.2 8.0 26.4 4.3 0.9 4.9 0.9 6.5 1.4 4.8 0.8 5.7 0.9 38.4 294.2 332.6 267.4 26.8 10.0 1.0 41.0 2.7 0.6 M3 S8 306 54.8 184.9 11.7 38.2 7.3 1.8 7.8 1.7 10.6 2.3 6.9 1.1 8.3 1.3 49.1 338.5 387.6 296.9 41.6 90.7 7.1 1.1 43.8 1.8 0.7 M3 S9 Avg 304.5 55.6 151.8 10.9 35.9 7.1 1.6 7.6 1.5 10.4 2.2 6.7 1.1 7.7 1.2 49.4 301.1 350.5 261.2 40.0 89.4 6.5 1.1 46.5 1.5 0.7 Mine 3 (Gouves) Profile 1 M3 S1 307.3 18.2 598.2 6.4 23.8 6.0 1.3 7.0 1.1 6.4 1.4 4.1 0.7 4.5 0.7 36.7 679.6 716.3 652.6 27.1 63.8 24.1 0.5 26.8 13.5 0.6 M3 S2 4.3 1.0 1.7 305.5 35.1 179.2 6.3 20.5 5.2 1.0 7.4 5.1 0.9 5.9 0.9 43.1 274.5 317.6 245.4 29.1 72.2 8.4 0.8 37.7 2.9 0.7 M3 S3 7.0 23.8 5.4 1.3 9.0 2.0 3.9 304 38.4 260.9 6.7 1.3 6.1 1.0 7.2 1.1 49.1 371.1 420.2 335.5 35.6 84.7 9.4 0.8 34.3 0.7 4.4 144.1 4.4 0.7 0.7 M3 S4 Avg 302.5 118.1 142.9 19.8 64.3 14.9 3.7 3.6 23.5 12.6 2.0 13.7 62.0 442.1 504.0 359.9 82.2 1.9 55.8 16.7 2.1 M3 S5 301 56.9 238.5 11.8 39.4 9.5 2.3 10.4 2.1 14.7 3.0 8.9 1.5 10.1 1.6 54.7 410.7 465.4 356.1 54.6 109.3 6.5 1.0 35.8 2.2 0.7 Mine 4 (Spartolakka) Profile 2 M4 S6 245.5 6.7 121.9 6.6 1.7 0.5 3.0 156.1 184.5 138.7 17.4 8.0 1.8 0.6 4.5 1.0 3.2 0.5 28.4 45.8 0.2 11.8 8.5 0.6 3.5 0.6 M4 S7 2.8 244 13.4 307.5 3.6 12.0 0.7 4.7 0.8 5.4 1.3 4.0 0.7 4.5 0.7 36.1 361.9 398.0 339.2 22.7 58.8 15.0 0.4 19.4 10.8 0.6 M4 S8 242.5 15.7 130.0 3.2 11.3 2.4 0.6 3.8 5.8 1.4 0.7 38.8 7.0 0.4 0.6 0.8 4.4 4.9 0.8 185.7 224.5 162.6 23.1 61.9 20.4 4.4 M4 S9 241 24.7 289.1 14.7 3.4 0.8 5.0 0.9 6.7 1.6 5.2 0.9 5.8 0.9 46.0 363.9 12.1 0.5 6.8 0.6 4.3 409.9 336.2 27.7 73.7 28.7 M4 S10 Avg 239.5 31.9 5.7 20.8 5.4 6.0 469.5 4.3 1.0 6.9 1.1 7.6 1.7 0.9 0.9 48.5 563.6 612.1 532.2 31.4 79.9 16.9 0.7 34.9 8.4 0.6 Mine 4 (Spartolakka) Profile 1 M4 S1 Avg 236.2 10.2 118.1 2.7 10.6 2.7 0.6 3.6 0.7 4.8 1.1 3.4 0.6 3.9 0.6 31.5 163.5 194.9 144.2 19.3 50.7 7.5 0.3 17.4 5.5 0.6 M4 S2 Ava 234.5 2.4 10.2 15.3 8.7 162.0 9.7 2.3 0.6 3.3 0.6 4.8 1.0 3.2 0.5 3.6 0.6 29.2 203.3 232.5 185.1 18.2 47.4 0.3 8.5 0.6 M4 S3 233 8.8 151.7 2.6 9.7 2.5 0.6 3.5 0.6 4.5 1.0 3.3 0.5 3.6 0.6 28.0 193.4 221.4 175.2 18.2 46.2 9.6 0.3 15.4 7.7 0.6 M4 S4 231.5 28.7 176.6 5.6 19.2 3.5 0.8 4.8 0.9 6.8 1.6 5.2 0.9 6.1 0.9 44.6 261.6 306.2 233.6 28.0 72.6 8.3 0.6 31.2 3.4 0.6 M4 S5 230 61.0 341.2 13.9 49.1 10.2 2.3 10.5 1.6 10.8 2.2 6.8 1.1 7.4 1.1 519.2 573.6 475.4 43.8 98.2 10.9 1.1 54.0 2.8 0.7 54.4 B3 Horizon Average 32.3 230.0 6.8 23.5 5.1 1.2 6.1 1.1 7.6 1.6 5.0 0.8 5.7 0.9 41.4 327.7 369.1 297.6 30.1 71.5 10.1 0.7 36.8 5.3 0.6

Table 6.2b. REE values (ppm) of all bauxite samples prepared using the lithium borate fusion – dissolution procedure. Blue values

indicate each element's highest value and values in red are each element's lowest value respectively.

Note: Samples with Avg indication represent the average element values of the original sample and its duplicates (sampling or/and ICP-MS duplicates). ΣLREE are La-Sm, ΣHREE are Eu-Lu, Ce/Ce\*=Ce<sub>N</sub>/(La<sub>N</sub>·Pr<sub>N</sub>)<sup>1/2</sup> and Eu/Eu\*=Eu<sub>N</sub>/(Sm<sub>N</sub>·Gd<sub>N</sub>)<sup>1/2</sup>, where Ce\* and Eu\* are the hypothetical concentrations that strictly trivalent Ce and Eu would have (Taylor and McLennan, 1985).



Figure 6.10. Relation of Co, V, Th and U to  $\Sigma REE+Y$  in bauxite.



Figure 6.11. Relation of Ce with LREE (upper) and HREE (middle) and relation between  $\Sigma$ HREE and  $\Sigma$ LREE (lower)

# 6.2.4 Optical Microscopy Results and Interpretation

Optical microscopy examination of bauxite samples revealed their texture (oolitic and pisolitic) composed mainly of boehmite/diaspore, hematite and the bauxitic matrix (Fig. 6.12 to 6.16). Optical differentiation of boehmite and diaspore is not feasible under the microscope. It was not possible to observe the remaining major minerals identified by XRD, which were goethite, anatase and kaolinite. This is possibly because they occur in low concentrations.



Figure 6.12. Photomicrographs in plane polarized reflected light of sample M1 S6. Diaspore (Ds) is the predominant mineral forming pisoliths while hematite (Ht) is mostly filling micro cracks and veins. Also weathered grains occur that usually are microcrystalline hematite particles intermixed with goethite and diaspore/boehmite.



Figure 6.13. Photomicrographs in plane polarized reflected light of sample M2 S6. Hematite (Ht) appears in pisoliths whereas diaspore (Ds) is the filling material. Pisoliths appear to be fragmented. Cracks that divided and displaced the parts of the pisolith were caused by tectonic events in the area. Whereas

multi fragmented areas indicate that the sample underwent plastic deformation from pressure of overlying layers or from blasting during bauxite mining.



Figure 6.14. Photomicrographs in plane polarized reflected light of sample M3 S1. Diaspore (Ds) is the predominant mineral and occurs in pisoliths. Hematite (Ht) mostly surrounds the diaspore pisoliths.



Figure 6.15. Photomicrographs in plane polarized reflected light of sample M3 S9. This sample is mainly composed of boehmite, and hematite, while diaspore is also present. Pisoliths of concentric layers have alternating AI-Fe composition. Onliths including weathered material fragments, which were transferred from another area, occur as well.



Figure 6.16. Photomicrographs in plane polarized reflected light of sample M3 S9. Hematite occurs in radial and euhedral crystals. Moreover, hematite appears in various alteration phases in grains or filling micro veins. Clastic grains and fragmented weathered material parts included in bauxite's matrix indicate that the material was transported from another area.
Considering all the optical microscope observations, the formation of bauxite and the mineral crystallization series can be described as:

- 1. Transportation of detrital minerals (including rare earth minerals), clastic grains and weathered material fragments/parts.
- 2. Deposition and *in situ* formation of ooliths/pisoliths.
- 3. Bauxitic matrix is filling empty spaces.
- 4. During the diagenesis stage bauxite is reformed.
- 5. Bauxitic material is filling cracks and veins caused by the pressure of overlying layers or tectonic activity.
- 6. This stage includes the crystallization of secondary minerals including REE.

# 6.2.5 SEM/EDS Results

The use of electron beam techniques such as SEM and EPMA offered the opportunity to observe minute mineral grains and receive information on their chemistry. The identified minerals are clay minerals (possibly kaolinite) (Fig. 6.17), anatase/rutile (Fig. 6.18), zircon (Fig. 6.19 and 6.20), barite (Fig. 6.21), pyrite (Fig. 6.22), chromite and magnesiochromite (Fig. 6.23), nickel (Fig. 6.24), hematite and goethite (Fig. 6.25 to 6.30) and rare earth minerals. These are mainly authigenic characterized by high Ce concentrations but some detrital minerals such as monazite were also identified.



Figure 6.17. BSE image of a clay mineral fragment (left) that is probably kaolinite found in M1 S6 polished block, which was made from the grinded sample, and its EDS spectrum (right).



Figure 6.18. BSE images of euhedral anatase/rutile (An) crystals (upper left and right) in sample M2 S6 and M3 S1 respectively and their EDS spectra (lower left and right).



Figure 6.19. BSE image showing zoned zircon crystal in sample M3 S1 and its EDS spectrum (right). The outer zone is enriched with Sc whereas in the center is Sc depleted (left). BSE image of a zircon crystal that contains small amounts of hafnium (sample M3 S9) and its EDS spectrum (right).



Figure 6.20. BSE images showing euhedral zircon (Zr) crystals in Al grains from M3 S1 polished block prepared from the grinded sample (up) and their EDS spectra (down). The right one also contains Sc and Th while the left one not.



Figure 6.21. BSE image showing barite crystal (left) occurring in sample M1 S6 and its EDS spectrum (right).



Figure 6.22. BSE image showing minute pyrite (Py) crystal (left) in sample M2 S6 and its EDS spectrum (right).



Figure 6.23. BSE images of chromite crystal (Cr) with small amounts of manganese in Al-rich matrix (left, M3 S9 sample) and magnesiochromite crystal (right, M4 S4 sample) near zircons (Zr) and their EDS spectra.



Figure 6.24. BSE image showing nickel crystal and its EDS spectrum in sample M4 S6.

Additionally, a more in depth observation of bauxite texture, mineralogy and matrix was carried out. In this context, it was observed that hematite occurs in various forms and shapes such as detrital grains, framboidal structures, euhedral crystals, pisoliths and altered crystals apart from filling veins (Fig. 6.25 to 6.30). Zircon occurs in three types: Sc-bearing also containing Th, Hf-bearing and pure zircon.



Figure 6.25. BSE image showing hematite grain (left) in sample M3 S1 and its EDS spectrum (right).



Figure 6.26. BSE images of intermixed hematite crystal alteration through the development of Fe microveins (M3 S1). Probably hematite is being replaced by goethite.



Figure 6.27. BSE images showing hematite (Ht) fragment in Al matrix (left). Goethite (Gt) fragment surrounded by hematite (right). Both minerals are iron oxides and produce the same spectra. Therefore their difference in color indicates that there are two different minerals and goethite is usually darker than hematite.



Figure 6.28. BSE images of hematite (white) with framboidal microstructure (spherical aggregates) in bauxite's matrix (black) in sample M3 S1 (left) and euhedral hematite (Ht) crystals (right) in sample M3 S9.



Figure 6.29. BSE image showing hematite crystals in sample M4 S4 and their EDS spectrum.



Figure 6.30. BSE images showing cracks towards the zones of a hematite pisolith meaning that it shrank because of dehydration (left, sample M4 S6), an unbroken grain (right, sample M4 S4) and their EDS spectra.

Finally, it was revealed that some parts of the matrix are composed of the main components of bauxite (Al, Fe and Ti) but also have significant amounts of Si (Fig. 6.31 and 6.32). Si is also intermixed with Al, Fe and Ti in microcrystalline particles. These "silica bars" are amorphous material appearing as crystal pseudomorphs. More precisely, this is possibly kaolinite that occurs locally and forms mixtures with Al hydroxides (as a result of kaolinization). Finally, it seems that most of the REE minerals occur near these high Si parts of bauxite, meaning that their formation may be related somehow with silica and these altered crystals.



Figure 6.31. BSE images of silica bearing pseudomorphs in sample M1 S6. In the left picture Si matrix with anatase/rutile (An), hematite (Ht) and zircon (Zr) crystals, whereas in the right picture coexists with AI matrix (black) and a REE (Ce-rich) crystal.



Figure 6.32. BSE image of Sc-bearing zircon crystal (Zr) hosted in Al, Si and Fe intermixed crystals in sample M4 S6 and their EDS spectra. The darker the color, the lower amounts of Fe occur.

# 6.2.6 SEM/EDS Results Regarding REE Bearing Minerals



Figure 6.33. Altered crystal in and around which occur more than fifteen Ce-rich crystals (sample M1 S6). Although REE minerals are not visible under the optical microscope, they appear as tiny bright white grains on the BSE image.

A=Picture of the polished block, B, C, D and E=Photomicrographs in plane polarized reflected light and F, G and H= BSE images.



Figure 6.34. BSE image of hematite pisolith, which is a part of the altered crystal of sample M1 S6 (Fig. 6.33) and chemical analysis of its zones. Centre (A) is composed of AI, Fe, Ti and Si material, zone B is composed mainly of AI, zone C is composed of hematite and zone D is a mix of Fe, AI and Si pseudomorphs. Hematite of zone C also hosts anatase/rutile crystals, which might also occur in zone (A) explaining the high Ti peak at the spectrum. High Ce minerals occur nearby in the diaspore (Ds) matrix.



Figure 6.35. Original (left) and secondary (right) zoomed BSE images of REE minerals in the altered crystal of sample M1 S6 (Fig. 6.33). REE minerals appear as very small and thin bright crystals near holes of the sample.



Figure 6.36. BSE images of high Ce, Ca and Th bearing oxides and their EDS spectra in sample M1 S6.



Figure 6.37. BSE images showing REE crystals in an Al matrix near a fractured hematite (Ht) grain in M2 S6 sample and their EDS spectra. The white arrows indicate the fracture direction. REE crystals are composed of Ce, Ca and maybe P.



Figure 6.38. BSE images of secondary Ce oxides crystallized in hematite (Ht) cracks either inside or in contact with the AI matrix (Sample M2 S6).



Figure 6.39. BSE images of Ce oxides developing in hematite veins in sample M3 S1 and their EDS spectra.



Figure 6.40. BSE images of Ce oxides in the form of aggregates in sample M3 S1. Fe peak is due to the background.



Figure 6.41. BSE image showing a Ce, La and Nd oxide without Ca and Th in sample M2 S1 and corresponding EDS spectrum.



Figure 6.42. BSE image and EDS spectrum of monazite (Mz) crystal in sample M1 S1.

As far as the REE bearing minerals are concerned, they occur in or nearby altered crystals, in micro veins or they fill holes, cracks and fissures (Figs. 6.33 to 6.40). These minerals are very high in Ce and their most important characteristic is that they also contain Ca and very low amounts of Th. Occasionally there are some peaks of Al, Fe, Ti and Si in their spectra, but these are more likely to be artifacts related to the volume of excitation of the SEM beam, which may include nearby or underlying minerals/matrix as the targeted spots are small and thin. This happens because the REE minerals are very small (usually about 10  $\mu$ m) and thin. These secondary minerals are authigenic and usually tend to appear as oxides. However, there are also Ce oxides without Ca that contain La and Nd (Fig. 6.41) and detrital monazite crystals (Fig. 6.42).

#### 6.2.7 SEM/EDS X-Ray Elemental Maps for REE Bearing Minerals

SEM elemental mapping (Fig. 6.43 to 6.57) in addition to the semiquantitative chemical analysis (Tables 10.17a to f) showed that REE bearing minerals are mainly composed of cerium (more than 50%), calcium (less than 5%) and thorium (less than 5%). Th does not appear in all analyzed crystals or might occur below SEM/EDS detection limits. Chemical analysis also indicates the presence of AI, Fe, Ti and Si. However, elemental mapping pictures proved that these elements do not occur in the REE crystals, but in the surrounding bauxite matrix/crystals. REE crystals are very small and thin, thus the SEM beam detects elements from the surrounding area. Finally, although some analysis show the presence phosphorus and fluorine in the REE crystals, both do not appear in all analysis, while their concentrations are extremely low, indicating that it is not very likely to occur. Semi-quantitative chemical analysis of some Ce oxide crystals is presented in Table 6.3. Totals are lower than 100% because AI, Fe, Ti and Si values were removed.



Figure 6.43. SEM/EDS pictures of REE minerals in sample M1 S6.



Figure 6.44. SEM/EDS elemental maps of a Ce oxide crystal in sample M1 S6. Al is the main matrix element. Fe, Ti and Si are distributed in all area, but Ti also is getting concentrated in anatase/rutile small crystals. Ce, Ca and Th are concentrated in the REE crystal and Ce is the predominant element.



Ca Ka1 Figure 6.45. SEM/EDS elemental maps of a Ce oxide crystal in sample M1 S6. Al is the main matrix element. Fe, Ti and Si are distributed in all area, but Ti also is getting concentrated in anatase/rutile small crystals. Ce and Ca are concentrated in the RE crystal and Ce is the predominant element.



Figure 6.46. SEM/EDS elemental maps of a Ce oxide crystal in sample M1 S6. Al is the main matrix element. Fe, Ti and Si are distributed in all area, but Ti is also concentrated in anatase/rutile small crystals. P is distributed everywhere

too, but its concentration is very low (close to the detection limits). Ce, Ca and Th are concentrated in the RE crystal and Ce is the predominant element.



Ce La1

Ca Ka1

Th La1

Figure 6.47. SEM/EDS elemental maps of a Ce oxide crystal in sample M1 S6. Al is the main matrix element. Fe, Ti and Si are distributed in all area, but Ti also is getting concentrated in anatase/rutile small crystals. P is distributed everywhere too, but its concentration is very low (close to the detection limits). Ce and Ca are concentrated in the RE crystal and Ce is the predominant element.

Table 6.3. SEM semi-quantitative chemical analysis for different points within REE bearing crystals in sample M1 S6.

		Cr	ystal 1			Crysta	12	Cr	ystal 3		Crys	stal 4	
Anal. No.	1	2	3	4	1	2	3	1	2	1	2	3	4
Element	Weight %												
Р								0.37	7		1.13	0.46	
Ca	3.41	1 2.8	3 2.72	2.72	3.22	2 3.33	3 3.56	6 2.4 <sup>-</sup>	1 2.9	9 2.77	2.36	2.95	2.25
Ce	72.65	5 62.18	3 58.29	62.04	68.02	69.29	9 59.6	1 63.3	60.5	65.55	62.21	68.42	64.49
Th	4.41	l 3.1'	1 3.9	1.91	1.3	3 3.4	4 3.37	7 0.82	2 1.4	6	0.53	1.24	1.04
0	15.55	5 18.67	7 19.31	19.79	18.14	17.71	19.69	9 20.93	3 20.1	3 20.86	20.69	18.4	19.95
Totals	96.02	2 86.76	84.22	86.46	90.68	3 93.73	8 86.23	8 87.83	8 85.0	6 89.18	86.92	91.47	87.73
		Crvs	stal 5				Crvs	stal 6					
Anal. No.	1	2	3	4	1	2	3	4	5	6			
Element					Weig	ht %				-			
Р						1.22							
Ca	2.07	1.51	2.45	2.34	3.03	3.1	2.87	2.74	2.77	2.57			
Ce	47.29	24.74	49.17	49.21	56.73	72.85	59.27	63.03	54.79	60.92			
Th	2.41	0.65	1.95	2.54	2.73	3.75	1.35	2.3	2.07	1.41			
0	24.24	26.28	25.05	23.08	19.01	16.54	21.45	19.11	20.4	18.49			
Totals	76.01	53.18	78.62	77.17	81.5	97.46	84.94	86.92	80.03	83.39			

#### 6.2.8 EPMA Results Regarding REE Bearing Minerals

Bauxite samples M1 S6, M2 S6 and M3 S1 were analyzed using an EPMA system (Fig. 6.48, Fig. 6.49, Table 6.4 and Table 10.18). Ce is the predominant element (65.718% on average and 8.842% standard deviation), while some REE crystals also appear to contain low amounts of Nd, Sm, Gd and Y. This is probably because Ce has major interferences on these elements. Ca occurs in all crystals in standard concentrations (5.742% on average and 2.357% standard deviation), Th is also present in most of the crystals analyzed, but U is absent or below detection limits. Finally, it is not likely for P and F to occur, which indicates that the rare earth minerals seem to be Ce oxides or carbonate minerals rather than fluorocarbonate or phosphate minerals that are mentioned in the literature (Maksimović and Pantó, 1996; Laskou and Andreou, 2003; Gamaletsos et al., 2011; Eliopoulos et al., 2014).

On the other hand, the absence of other REE indicates that these minerals are unlikely to be Ca containing hydroxylbastnäsites-Ce (Ce(CO<sub>3</sub>)(OH)) with all of their F content being replaced by OH, although Ca containing hydroxylbastnäsite-Nd and La ((Nd,La)CO<sub>3</sub>(OH,F)) occurrences have been reported by Lymperopoulou (1996) and Ochsenkühn-Petropoulou et al. (1996) in the lowermost parts of the Mandri-Tsakni bauxite deposit of the third bauxite horizon. As a result the low totals (73.356% on average and 10.030% standard deviation) may be explained by the absence of carbon that cannot be measured by SEM and EPMA because samples have to be carbon coated for the analysis.



Figure 6.48. BSE pictures of an altered REE bearing crystal in sample M1 S6.

Table 6.4. Quantitative EPMA data for REE crystals in samples M1 S6, M2 S6 and M3 S1. Values in red color are unreliable because they are very close to the detection limits or they interfere with Ce. Therefore they were not considered for the estimation of totals.

Sample				M1 S6			M2	S6	M2 S6				
Comment	M1-1	M1-1	M1-2	M1-3	M1-4	M1-5	M1-6	M2-7	M2-8	M2-9	M2-10	M3-1	
Anal. No.	5	15	6	7	8	9	10	11	12	13	14	16	
CaO	3.106	7.295	2.536	2.699	2.856	7.902	7.289	6.101	7.219	6.692	5.772	9.432	
F	1.569	0	1.109	0	1.111	0	0	0	0	0	0	0	
P <sub>2</sub> O <sub>5</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
ThO <sub>2</sub>	4.198	4.539	0	3.970	4.178	1.588	4.279	0	0	0	0.199	0	
UO <sub>2</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Sc <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Y <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0.247	0.213	0	0	0	
La <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
	70.399	75.149	66.455	67.451	70.271	58.273	73.310	41.560	65.275	62.797	68.680	68.995	
Pr <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Nd <sub>2</sub> O <sub>3</sub>	0.896	0.792	0	0	0.666	0.434	0.569	0.588	0.660	0.659	0.850	0.656	
Sm <sub>2</sub> O <sub>3</sub>	0.506	0.588	0	0	0	0	0.669	0	0.395	0.330	0.487	0	
Eu <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Gd <sub>2</sub> O <sub>3</sub>	4.467	0	0	4.029	4.229	4.382	0	0	0	0	0	0	
Tb <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
$Dy_2O_3$	0	0	0	0	0	0	0	0	0	0	0	0	
Ho <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Er <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Tm <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Yb <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Lu <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	0	0	
Total	77.703	86.983	68.991	74.120	77.305	67.763	84.878	47.661	72.494	69.489	74.452	78.427	



Figure 6.49. Various BSE images of REE bearing crystals in samples M1 S6, M2 S6 and M3 S1.

### 6.3 Mineralogy and Geochemistry of Red Mud Waste

# 6.3.1 XRF Analysis for Red Mud Waste Samples

The most important feature of the XRF analysis of red mud waste samples is that the semi-quantitative totals are significantly low (Table 6.5). This is mainly because the really low Fe values appear low compared to comparative analyses provided by the Aluminium S.A. However, if  $Fe_2O_3$  is treated as a balance compound instead of a measured (i.e. all other constituents are measured and the remaining sum is made up to 100% by the iron oxide) then the percentages would be approximately 42-44%, which would be more in line with the Aluminium S.A. averages.

Table 6.5. Semi-quantitative chemical composition of red mud waste samples and Aluminium S.A. average red mud composition.

Wt.%	SqA S4	SqB S4	SqZ S C2	Average	Aluminium S.A. Average
Al <sub>2</sub> O <sub>3</sub>	15.70	16.60	15.80	16.03	11 - 23
Fe <sub>2</sub> O <sub>3</sub>	21.06	20.60	21.71	21.12	38 - 50
TiO <sub>2</sub>	5.94	5.58	6.12	5.88	5 - 8
SiO <sub>2</sub>	6.48	5.53	7.18	6.40	4 - 15
CaO	10.18	9.76	9.77	9.91	4 - 12
SO₃	1.36	1.75	0.84	1.32	
MnO	0.07	0.04	0.03	0.05	
MgO	0.18	0.21	0.18	0.19	
Na <sub>2</sub> O	3.82	3.87	4.00	3.90	1.8 - 4
$P_2O_5$	0.14	0.13	0.09	0.12	
K <sub>2</sub> O	0.14	0.16	0.10	0.13	
CI	0.11	0.10	0.12	0.11	
LOI	13.40	12.70	10.90	12.33	
Total	79.11	77.59	77.45		
ррт					
$Cr_2O_3$	1270	1390	1480	1380	
NiO	409	496	553	486	
$V_2O_5$	1690	1850	2150	1897	
ZrO	749	724	832	768	
Nb <sub>2</sub> O <sub>5</sub>	71	68	80	73	
SrO	76	60	62	66	
CeO <sub>2</sub>	1000	1100	940	1013	

Note: The results are not normalized to 100%. Values in grey italics were quantified with exactly the same method used for the rest of the elements, but not definitively identified as present by the software. This is due to the small peak height and shape that is debatable on whether or not the indication can be 100% interpreted as element's presence. Zero valued elements or other missing trace elements are below XRF detection limits, which are from % to ppm but are also element, sample and mode dependent.

Apart from Fe, red muds are mainly composed of Al, Ti, Si, Ca and S oxides. Minor elements are Mn, Mg, Na, P, K and Cl, whereas, Cr, V, Ni and Zr are the most important trace elements. Furthermore, all samples indicate high Ce values. The loss on ignition is same with bauxite, approximately 12%. Al is significantly lower compared to bauxites as a result of the Bayer process. Hence, all the other elements and especially Fe are found in higher concentrations as expected, compared to the initial bauxite. Ca high values are more likely due to calcination during Bayer process, rather than only originating from bauxite.

# 6.3.2 Trace Elements and REE Results of Red Mud Waste Samples

Trace and rare earth element content of red mud waste samples were calculated by using the lithium borate fusion dissolution procedure. All trace and REE values appear higher than bauxite, meaning that red mud samples are enriched compared to bauxite (Fig. 6.50). Again V and Zr are found in high concentrations as already shown in the XRF data. But, apart from V, Zr and REE, there are no significant variations in element concentrations between red mud waste samples observed. V and Zr are found in very high concentrations in bauxite. Hence, even if their enrichment factor (red mud waste to the initial bauxite) is the same as the other elements, their high concentrations make their differences higher. Red mud waste's average concentration shows no significant variations. This is not unexpected as red mud waste represents mixed bauxite that passed through Bayer process resulting in a blended homogeneous by-product.



Figure 6.50. Pie charts showing the average trace element (left) and REE (right) concentration percentages of red mud waste.

W concentration in red mud waste is lower than in bauxite samples. However, the W values in red mud waste are the real ones as the samples were prepared by using agate mortar (rather than tungsten ring mill for bauxite samples) and the contamination was avoided (Table 6.6a).

Table 6.6a. Trace element values (ppm) of red mud waste samples prepared using the lithium borate fusion – dissolution procedure.

	SQA S4	SQZ SC2	SQB S4 Avg	Average
Ba	94.0	79.0	94.5	89.2
Be	4.0	6.0	4.5	4.8
Со	48.2	53.3	47.7	49.7
Cs	1.3	1.7	1.2	1.4
Ga	45.2	40.5	49.2	45.0
Hf	28.3	30.6	27.0	28.6
Nb	86.4	95.4	81.6	87.8
Rb	5.9	4.2	5.5	5.2
Sn	19.0	21.0	18.0	19.3
Sr	145.1	113.2	109.6	122.6
Та	6.7	7.2	6.4	6.8
Th	86.9	95.6	83.3	88.6
U	10.8	13.5	12.6	12.3
V	852.0	974.0	934.5	920.2
W	26.2	21.4	43.2	30.3
Zr	1001.9	1089.5	941.5	1011.0

As far as the REE concentrations in red muds are concerned, there are no significant differences between samples observed, just like the other trace elements determined in bauxites. Additionally, REE values are higher than bauxites, representing enriched concentrations of the mixed bauxite ore derived from different mines.  $\Sigma$ REE varies between 734.8 and 790 ppm with an average concentration of 769.3 ppm while  $\Sigma$ REE+Y ranges between 827.9 and 896.2 ppm and the average is 867.5 ppm (Table 6.6b).

The average  $\Sigma LREE/\Sigma HREE$  ratio is 8.8. Ce generally covers about the 48% of the total REE and its percentage is significantly decreased compared to bauxite that was 62%. Ce is followed by La (15%), Nd (12%) and Y (11%). Their values seem to be increased in comparison with bauxite where average Y was 11%, La was 9% and Nd 6% respectively. This fact again can be explained due to the heterogeneity of bauxite. Hence, if this study's collected bauxite samples were passing through Bayer process, REE proportions percentages would be definitely closer.

Table 6.6b. REE values (ppm) of red mud waste samples prepared using the lithium borate fusion – dissolution procedure.

	SQA S4	SQZ SC2	SQB S4 Avg	Average
La	134.9	129.3	117.8	127.3
Се	416.9	421.0	395.9	411.3
Pr	29.5	28.3	27.1	28.3
Nd	107.4	104.0	100.3	103.9
Sm	20.5	20.5	19.3	20.1
Eu	4.6	4.4	4.3	4.4
Gd	19.3	19.6	17.9	18.9
Tb	3.1	3.0	2.9	3.0
Dy	19.8	19.9	18.7	19.4
Но	4.1	4.0	3.7	3.9
Er	12.5	11.9	11.1	11.8
Tm	2.0	2.0	1.8	1.9
Yb	13.4	13.5	12.1	13.0
Lu	2.1	2.1	1.9	2.0
Υ	106.2	95.2	93.2	98.2
ΣREE	790.0	783.2	734.8	769.3
ΣLREE	709.3	703.1	660.4	690.9
ΣHREE	80.8	80.2	74.4	78.4
<b>ΣLREE/ΣHREE</b>	8.8	8.8	8.9	8.8
ΣREE+Y	896.2	878.4	827.9	867.5
ΣHREE+Y	187.0	175.4	167.5	176.6

The choice of the three red mud waste samples prepared using the lithium borate fusion – dissolution procedure, was based on two factors. Firstly there was chosen one sample from each red mud depositional plateau. Secondly, based on the preliminary results of the multi-acid attack method (Table 6.7a and b), the highest, lowest and average REE samples were selected. As a result, samples SQZ SC2 and SQB S4 appeared to be the highest and the lowest in REE content respectively, while Sample SQA S4 was selected as an average one in order to represent the Square A depositional plateau. Finally, Table 6.8 contains the red mud waste to bauxite enrichment factor (ratio) for all elements. These were calculated from the average trace element concentrations of all bauxite and red mud waste samples prepared using the lithium borate fusion – dissolution procedure. Both tables show that the vast majority of the enrichment factors for red mud waste samples to bauxite, for all elements (including rare earths), are higher than 1. This happens because it seems that all trace elements and REE pass through the alumina extraction process and end up in red mud waste.

Sample Name	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	w	Zn	Zr
SqA S1	0.6	232.8	85.8	5.6	6.9	0.8	47.6	1610.9	53.0	65.0	18.2	31.2	42.5	125.6	685.4	113.7	3.0	39.5	133.6	33.4	88.2	8.8	868.4	65.8	68.1	892.1
SqA S2	0.5	238.8	92.3	5.7	5.4	0.7	51.4	1746.4	58.0	67.6	19.3	27.5	35.3	114.8	726.8	120.0	2.3	29.5	147.4	22.9	77.8	9.2	920.6	49.2	71.2	939.2
SqA S3	0.6	211.6	91.1	7.4	5.0	0.9	49.3	1563.9	51.0	68.7	19.0	24.2	28.3	100.6	661.1	116.0	4.0	24.4	137.5	17.5	72.5	10.4	752.2	33.6	63.9	850.8
SqA S4	0.6	231.2	98.7	6.0	5.3	0.9	55.5	1695.3	48.3	72.8	20.4	26.4	35.9	108.2	765.9	130.7	4.9	27.5	149.3	17.4	79.6	11.2	832.1	40.1	69.1	925.4
SqB S1	0.6	234.1	89.6	8.2	4.6	1.0	48.0	1723.2	44.6	63.5	18.6	24.9	24.4	101.4	925.8	119.0	1.3	29.0	106.5	14.8	65.8	8.9	978.0	43.3	52.9	883.1
SqB S2	0.6	234.1	94.8	6.3	4.8	0.9	51.2	1794.7	44.5	71.8	19.9	25.8	21.5	103.5	950.3	125.3	1.8	28.5	114.5	14.5	78.1	10.7	1025.0	43.0	58.1	926.3
SqB S3	0.6	246.6	97.8	10.5	4.9	0.8	53.6	1707.4	45.6	71.7	18.6	24.5	22.5	98.3	941.6	126.1	2.9	29.4	116.3	13.6	78.1	11.7	963.9	43.7	61.5	878.5
SqB S4	0.6	237.3	95.2	5.7	4.4	0.9	46.8	1680.9	42.2	70.3	16.9	24.8	38.1	97.9	857.8	110.8	1.9	29.0	95.6	13.1	69.2	10.4	890.6	45.4	51.2	881.0
SqZ S A1	0.6	215.9	80.6	6.7	4.5	0.6	60.5	1440.4	39.2	62.0	18.4	22.3	17.4	103.6	1002.6	127.2	3.1	28.0	110.5	12.8	78.4	10.9	1028.6	34.3	47.3	791.5
SqZ S A2	0.6	218.5	83.2	6.0	4.7	0.8	61.7	1418.8	38.2	62.4	19.6	21.9	16.4	102.8	1006.9	129.6	3.4	27.7	113.0	12.0	79.6	11.3	1032.2	34.3	43.3	793.2
SqZ S A3	0.4	223.3	80.9	6.2	5.1	0.5	62.3	1535.3	32.4	65.0	19.1	25.0	18.8	127.2	1031.2	128.4	2.1	36.3	116.0	17.0	83.7	10.8	1009.1	43.7	34.0	814.7
SqZ S B1	0.3	191.8	89.5	5.2	5.0	0.5	68.2	1687.5	46.1	66.8	20.3	25.6	16.9	123.2	1107.6	132.7	3.1	32.1	111.3	13.7	88.9	12.3	932.5	29.6	61.0	923.2
SqZ S B2	0.3	190.5	94.1	8.8	4.9	0.3	69.1	1685.3	44.9	67.7	21.3	25.8	16.8	119.9	1120.3	135.0	4.6	30.9	115.3	13.3	92.5	12.6	982.4	27.0	63.8	932.9
SqZ S B3	0.3	192.3	94.5	5.3	4.7	0.5	68.6	1690.2	44.6	68.0	19.9	25.2	16.3	118.4	1101.5	132.2	4.2	30.3	112.2	12.4	92.8	12.5	964.4	26.0	58.9	924.0
SqZ S C1	0.3	193.2	89.0	5.4	4.5	0.3	56.8	1619.6	39.3	62.1	19.1	23.1	15.4	112.7	938.2	127.2	2.3	30.2	116.4	11.6	83.8	11.6	936.4	21.8	45.4	855.4
SqZ S C2	0.2	199.0	96.8	5.5	4.9	0.4	62.7	1782.5	45.4	69.8	21.0	24.8	16.7	120.4	997.3	139.2	3.9	31.2	125.9	12.3	92.2	12.9	983.4	24.9	55.1	915.9
SqZ S C3	0.2	195.1	91.4	6.1	4.7	0.6	61.6	1768.1	41.0	69.8	20.5	24.5	16.0	116.8	979.2	135.6	3.0	31.5	121.3	11.7	89.7	12.4	960.2	23.1	48.3	910.5
SqZ S C4	0.2	193.1	89.8	5.6	4.6	0.4	60.0	1710.4	41.2	65.1	20.3	23.5	15.8	113.4	950.4	133.2	3.2	30.7	115.2	11.2	87.2	12.2	980.2	22.2	50.4	878.5
Average	0.5	215.5	90.8	6.5	4.9	0.7	57.5	1658.9	44.4	67.2	19.5	25.0	23.0	111.6	930.6	126.8	3.1	30.3	119.9	15.3	82.1	11.2	946.7	36.2	55.7	884.2

Table 6.7a. Trace element values (ppm) of all red mud waste samples prepared using the multi-acid attack - dissolution

procedure.

Table 6.7b. REE values (ppm) of all red mud waste samples prepared using the multi-acid attack – dissolution procedure.

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y	ΣREE	ΣLREE	ΣHREE	<b>ΣLREE/ΣHREE</b>	ΣREE+Y	ΣHREE+Y	ΣREE+Y+Sc
SqA S1	91.7	109.9	347.7	25.8	95.1	18.2	4.0	14.9	2.7	15.6	3.4	9.9	1.7	11.0	1.8	74.1	661.7	596.7	65.0	9.2	735.8	139.1	827.5
SqA S2	100.0	122.0	380.7	29.3	107.1	21.1	4.5	16.9	3.1	17.8	3.7	11.2	1.9	12.6	2.0	83.3	733.9	660.2	73.7	9.0	817.2	157.0	917.2
SqA S3	90.7	126.1	386.3	29.4	107.5	20.9	4.6	16.7	3.2	16.8	3.7	10.4	1.9	11.5	2.0	79.3	741.0	670.2	70.8	9.5	820.3	150.1	911.0
SqA S4	99.0	134.3	421.1	30.5	112.3	21.2	4.6	17.5	3.3	18.0	3.8	11.2	2.0	12.4	2.1	84.3	794.3	719.4	74.9	9.6	878.6	159.2	977.6
SqB S1	87.0	89.7	312.1	23.2	87.4	17.5	4.0	14.6	2.8	15.6	3.3	9.8	1.8	11.0	2.0	68.8	594.8	529.9	64.9	8.2	663.6	133.7	750.6
SqB S2	100.6	107.7	383.1	27.1	102.2	20.3	4.5	17.1	3.2	17.5	3.8	11.3	2.0	12.3	2.1	81.2	714.2	640.4	73.8	8.7	795.4	155.0	896.0
SqB S3	99.4	122.2	405.7	29.5	110.6	21.3	4.7	17.6	3.3	18.0	3.8	11.0	1.9	12.1	2.1	83.5	763.8	689.3	74.5	9.3	847.3	158.0	946.7
SqB S4	82.2	81.5	336.0	21.9	82.7	17.2	3.9	14.3	2.7	14.9	3.3	9.3	1.8	10.3	1.9	64.8	601.7	539.3	62.4	8.6	666.5	127.2	748.7
SqZ S A1	100.5	130.3	367.1	30.1	112.8	22.6	4.9	19.4	3.5	20.0	4.1	11.9	2.1	12.7	2.2	89.9	743.7	662.9	80.8	8.2	833.6	170.7	934.1
SqZ S A2	98.5	138.6	373.9	32.1	120.6	24.0	5.2	20.5	3.7	20.2	4.2	12.0	2.1	13.1	2.2	90.3	772.4	689.2	83.2	8.3	862.7	173.5	961.2
SqZ S A3	99.9	126.9	369.5	29.7	111.9	22.0	4.7	18.6	3.3	19.1	3.9	11.3	1.9	12.0	1.9	83.3	736.7	660.0	76.7	8.6	820.0	160.0	919.9
SqZ S B1	103.3	123.5	411.7	28.9	106.8	21.7	4.4	18.2	3.0	18.4	3.6	11.1	1.7	12.0	1.7	87.3	766.7	692.6	74.1	9.3	854.0	161.4	957.3
SqZ S B2	108.8	127.1	433.2	30.0	111.9	22.7	4.8	19.6	3.2	20.1	3.9	11.8	1.9	12.8	1.9	95.3	804.9	724.9	80.0	9.1	900.2	175.3	1009.0
SqZ S B3	111.0	126.8	437.0	29.8	114.1	22.8	4.7	19.5	3.3	20.2	3.9	11.9	1.8	13.1	1.9	96.7	810.8	730.5	80.3	9.1	907.5	177.0	1018.5
SqZ S C1	112.1	123.0	398.0	29.1	105.6	21.5	4.4	17.8	3.0	19.5	3.8	11.5	1.8	12.8	1.9	87.7	753.7	677.2	76.5	8.9	841.4	164.2	953.5
SqZ S C2	120.8	141.5	463.2	33.4	123.4	24.3	5.1	20.2	3.4	21.1	4.2	12.4	2.0	13.6	2.1	96.5	869.9	785.8	84.1	9.3	966.4	180.6	1087.2
SqZ S C3	120.4	138.0	444.1	32.1	117.8	23.6	4.9	19.4	3.3	20.5	4.1	12.4	1.9	13.6	2.0	93.7	837.7	755.6	82.1	9.2	931.4	175.8	1051.8
SqZ S C4	112.0	130.3	438.0	30.2	112.6	22.4	4.6	18.8	3.2	19.8	4.0	11.9	1.9	13.1	2.0	91.7	812.8	733.5	79.3	9.2	904.5	171.0	1016.5
Average	102.1	122.2	394.9	29.0	107.9	21.4	4.6	17.9	3.2	18.5	3.8	11.2	1.9	12.3	2.0	85.1	750.8	675.4	75.4	9.0	835.9	160.5	938.0

Note: Blue values are each element's highest value and values in red are each element's lowest value respectively.

	Ded Mud	Bouvito	Datia		Red Mud	Bauxite	Datia
	Rea Mua	Dauxite	Ratio		(n=3)	(n=37)	Ratio
Ba	89.2	70.4	1.3	La	127.3	32.3	3.9
Be	4.8	3.8	1.3	Се	411.3	230	1.8
Со	49.7	44.2	1.1	Pr	28.3	6.8	4.2
Cs	1.4	0.4	3.5	Nd	103.9	23.5	4.4
Ga	45.0	56.6	0.8	Sm	20.1	5.1	3.9
Hf	28.6	13.8	2.1	Eu	4.4	1.2	3.7
Nb	87.8	50.7	1.7	Gd	18.9	6.1	3.1
Rb	5.2	1.4	3.7	Tb	3.0	1.1	2.7
Sn	19.3	11.6	1.7	Dy	19.4	7.6	2.6
Sr	122.6	41.9	2.9	Но	3.9	1.6	2.4
Та	6.8	4.3	1.6	Er	11.8	5.0	2.4
Th	88.6	52	1.7	Tm	1.9	0.8	2.4
U	12.3	7.8	1.6	Yb	13.0	5.7	2.3
V	920.2	632.8	1.5	Lu	2.0	0.9	2.2
W	30.3	106.2	0.3	Υ	98.2	41.4	2.4
Zr	1011.0	498	2.0	ΣREE	769.3	327.7	2.3
				ΣLREE	690.9	297.6	2.3
				ΣHREE	78.4	30.1	2.6
				<b>ΣLREE/ΣHREE</b>	8.8	10.1	0.9
				ΣREE+Y	867.5	369.1	2.4
				ΣHREE+Y	176.6	71.5	2.5

Table 6.8. Average concentrations (ppm) of trace elements and REE in red mud waste and bauxite samples and their red mud waste to bauxite enrichment factors.

The average enrichment factor of the trace elements is close to 2.0. W enrichment factor is 0.3 showing clearly the contamination during preparation of bauxite samples, comparing to the red mud waste samples that are uncontaminated. Also Ga enrichment factor is slightly below 1 (it is 0.8). Zr and Hf are enriched in red mud as all zirconium crystals are difficult to dissolve and consequently pass to red mud doubling their abundance (Fig. 10.26). V and Sr are enriched in red mud as well. The rest of the elements are also enriched but their concentrations are low.

As far as the REE and yttrium are concerned, their average enrichment factor is 3.0 (Table 6.8 and Fig. 6.51), which is significantly higher than 2 that suggested by Ochsenkühn-Petropoulou et al. (1994). Additionally, it is worth mentioning that the high average enrichment factors for La, Pr, Nd, Sm, Eu, Gd are more than 3, which means that bauxite samples of this study have lower amounts of these elements compared to the mixed bauxite used for the alumina production. On the other hand, Ce enrichment factor is 1.8, meaning that this study's bauxites contain high amounts of cerium, and maybe much more than bauxite's average.



Figure 6.51. Plot of average chondrite normalized REE values for B3 underground bauxite mines and dehydrated red mud waste using McDonough and Sun (1995).

### 6.4 REE Leaching Experiments

### 6.4.1 REE Leaching from the Greek Red Mud Waste

From the literature, Greek bauxite contains approximately 500 ppm of REE on average while red mud contains double the amount (1000 ppm). The enrichment factor for rare earths in red mud compared to bauxite is about a factor of two (Ochsenkühn-Petropoulou et al., 1994). In addition, Greek red mud contains approximately 130 ppm of scandium compared with 390 ppm in Jamaican bauxite. The relatively high REE (including scandium and yttrium) content (~1000 ppm) in the red mud indicated the need for REE extraction methods in order to become an alternative REE resource. This is because Greek bauxite and red mud contains significantly lower REE contents compared

to other well-known commercial REE deposits such as Mountain Pass (8.24% REO), Mount Weld (8.1% REO) and Bayan Obo (4.1% REO) (Wall, 2014). Whereas, other REE resources with lower REE concentrations are the Jamaican red muds (0.23-0.38 wt.%  $\Sigma$ REE+Y) and the Chinese HREE rich ion adsorption deposits (0.03-0.35% REO) (Mariano and Mariano, 2012; Wall, 2014).

During the mid-nineties, the first leaching efforts by Greek scientists resulted from research on acidic leaching followed by ion exchange separation. In more detail, metal leaching through different acids (HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>), different acid concentrations and different leaching conditions proved that best REE recovery was a result of 0.5 M HNO<sub>3</sub> leaching at ambient temperatures and pressures ( $25^{\circ}$  C for 24 h) with a liquid-to-solid (L/S) ratio of 50:1. The specific protocol recovered 96% of yttrium, 80% of scandium and lower amounts from HREE to LREE: heavy (70% of Ytterbium, 60% of Erbium and 52% of Dysprosium), middle (53% of Europium, 52% of Neodymium, 49% of Gadolinium and Samarium) and light lanthanides (35% of Lanthanum and Praseodymium and 29% of Cerium) (Lymperopoulou, 1996; Ochsenkühn-Petropoulou et al., 1996). In this context, leaching via dilute HNO<sub>3</sub> was performed at pilot scale and optimized for the extraction of scandium from red mud waste (Ochsenkühn-Petropoulou et al., 2002).

This protocol seems interesting but cannot provide a feasible production of REE oxides even if has very good recovery values of Sc and Y (120 and 95 ppm on average). It provides low recoveries of Ce, La and Nd that are the predominant elements (430, 130 and 100 ppm on average respectively) (Table 6.9). Nowadays, REE leaching by using various acidic liquids, being researched by IOF-KP RARE<sup>3</sup> project (Rao Borra et al., 2015), produced much better results compared to the previous method, resulting in around 70–80% REE recovery from the leaching of bauxite residue by using 6 N HCl for 24 h duration at temperature of 25° C with 50:1 liquid-to-solid (L/S) ratio. It was also noticed that REE extraction increased with acid concentration, time and L/S ratio.

Apart from acidic liquid leaching techniques, a bench scale extraction of REE from dehydrated red muds by using imidazolium based ionic liquids is currently being researched through the EURARE project at National Technical University of Athens (NTUA) (Davris et al., 2014; Bourbos et al., 2014).

Table 6.9. Concentration (ppm) of REE in Greek red mud batches. RM 1993-2012 is from Ochsenkühn-Petropoulou (2014), RM 2015 is from Rao Borra et al., (2015), RM BP is from this study's red mud waste literature review and RM N is from this study's red mud results using the lithium borate fusion dissolution procedure.

	RM 1993	RM 2001	RM 2007	RM 2012	RM 2015	<b>RM BP</b>	RMN
La	149	101.5	132.0	147.6	114.0	150.6	127.3
Ce	418	404.0	492.0	498.0	368.0	421.6	411.3
Pr					28.0	25.6	28.3
Nd	115	86.3	88.5	92.5	98.6	120.9	103.9
Sm	28.9	20.5	22.0	24.3	21.3	29.1	20.1
Eu	5.0	3.7	4.0	4.9	5.0	5.0	4.4
Gd	23.3	23.4	20.5	21.3	22.0	23.3	18.9
Tb					3.5		3.0
Dy					16.7	14.4	19.4
Но					3.9	4.3	3.9
Er	12.2	12.7	13.1	10.9	13.5	17.2	11.8
Tm					1.9		1.9
Yb	15.6	15.0	14.4	15.8	14.0	15.6	13.0
Lu					2.4	2.4	2.0
Υ	91.2	94.0	94.0	115.0	75.7	93.1	98.2
Sc	127.9	107.0	130.0	110.0	121.0	119.4	
ΣREE	767.0	667.1	786.5	815.3	712.8	830.0	769.3
ΣREE+Y	858.2	761.1	880.5	930.3	788.5	923.1	867.5
ΣREE+Y+Sc	986.1	868.1	1010.5	1040.3	909.5	1042.5	

Finally, current advances in the valorization of red muds for minor metals include the development of Rusal's pilot plant in the Urals, Russia, which is capable of producing 2.5 tons per annum of primary scandium oxide concentrate (press release, RUSAL 21/08/2014). The commercial extraction of REE from red muds has been further advanced by the granting of patents in both Canada and the US to Orbite Aluminae for the 'Orbite Process' (the two patents are Canadian patent 2,857,574 and U.S. patent 14/371,364, press release, 05/05/2015), which uses red muds as a feedstock for a new beneficiation stream which aims to extract REE and other minor metals along with alumina, magnesium oxide and titanium dioxide from the residue. It is thus clear that red muds have the potential to be a source of REE for the European economy.

#### 6.4.2 Results of the REE Leaching Tests

In order to investigate the potential presence of adsorbed REE cations in bauxite and red mud waste Protocol D of Sanematsu et al. (2013) was tested (Table 5.3). Apart from Greek bauxite and red mud waste samples leaching tests were also applied at Jamaican bauxite and red mud waste samples, Mount Weld (Australia) laterite samples and kaolinites. The selection of a large range of sample types was in order to assess what may control the leaching of exchangeable REE. These tests took place at CSM, while the same Protocol D was also applied on the same samples at the BGS labs, Keyworth.

Data from the BGS leaching experiments, which were carried out using the ammonium sulphate leaching of exchangeable cations protocol, following the recipe of Sanematsu et al. (2013), are plotted on the chondrite normalized graph in Figure 6.52. All the results appear quite low and none reach the 500 ppm leachable REE that is required by Bao and Zhao (2008) to satisfy the definition of ion adsorption ore. Additionally, the order of concentrations of leachable cations is not as expected. Highest were the two Greek bauxite samples (M1 S1 and M2 S6) that are enriched in light REE and with approximately 600 ppm total REE. Second were the kaolinite samples, showing release of heavy REE. Highest heavy REE were in samples H and G. F and I also had high Y but lower HREE in the leach solution. Surprisingly, the lowest values were from the Chinese samples. This fact means that these samples may come from a non-prospective part of the profile or they have already been leached. However, if stronger acids were applied on all samples maybe more REE could be released.

The leaching results by applying the Protocol D at CSM labs were significantly lower compared to the Sanematsu et al. (2013) protocol BGS results (Fig. 6.53). This may caused by the fact that during the experiment there was a problem in counting and adjusting the pH, possibly due to the heterogeneity of the samples. This problem was more intense with the Greek and Jamaican red mud waste samples. The pH probe couldn't stabilize at a certain value, so the pH values noted were approximate. Moreover, there was an accident during the filtering of M1 S1 sample; hence its results are not accurate (Table 6.10).



Figure 6.52. Graphs showing the results of the BGS leaching tests (upper graph), compared with those from Bao and Zhao (2008) and Sanematsu et al. (2013) (middle graph) and Mariano and Mariano (2012) chondrite normalized

REE concentrations in Jamaican red mud (top group) and China ion adsorption clay samples (lower group) (lower graph).



Figure 6.53. Chondrite normalized values of REE from various samples including Greek (M1 S1, M2 S6 and M3 S4 Dupl) and Jamaican (JB1 and 2) bauxites and red mud waste (Sq Z C2 and RM 1 respectively), Australian laterites (Mt. Weld) and UK clays (Kaolin) after being leached using protocol D at CSM labs.

Sample	Sample Weight	рΗ	$H_2SO_4$	Final pH	Room Temp.
M1 S1	0.99439	6.49	10 µl	4.850	21.8 °C
M2 S6	0.99707	6.47	10 µl	4.680	21.8 °C
SQ Z C2	0.99726	7.35	130 µl	4.901	21.8 °C
SQ Z C2 Dupl.	0.99892	7.67	350 µl	4.847	21.8 °C
JB1 Gray	0.99394	6.56	10 µl	3.600	21.8 °C
JB1 Gray Dupl.	0.99543	5.95	10 µl	4.540	21.8 °C
JB2 Red	1.00104	6.60	10 µl	4.550	21.8 °C
RM 1 (Jamaica)	0.99841	7.55	300 µl	4.680	21.8 °C
Mt. Weld Avg.	0.9998	6.32	20 µl	4.150	21.8 °C
Mt. Weld Bottom	0.99823	6.55	30 µl	3.870	21.8 °C
Mt. Weld Bottom Dupl.	1.00013	6.54	20 µl	4.330	21.8 °C
M3 S4 Dupl.	0.99905	6.47	10 µl	4.720	21.8 °C

Table 6.10. Sample preparation details for the leaching protocol D at CSM labs.



Figure 6.54. Chondrite normalized REE diagrams for REE leached from Greek bauxite and red mud waste samples by using the protocol D at CSM labs (upper graph) and compared to the BGS leaching results using the same protocol (lower graph).

Figure 6.54 clearly shows that this protocol works best for the Mount Weld samples that are very enriched in REE, and especially in the leaching of LREE. It can also leach small amounts of LREE from Greek bauxite samples

but it surprisingly gives even lower results at Greek red muds, which contain higher amounts of REE. On the other hand, unlike to Greek samples, Jamaican red mud waste sample shows bigger REE recovery values compared to the Jamaican bauxites. Additionally, the red bauxite sample appears to be more enriched in comparison with the gray one, while both bauxite samples show higher leaching values for the HREE. Finally, the leaching results of kaolinite samples are very low apart from Kaolin G sample, but leaching was more successful for the HREE. At this point it is worth mentioning that the kaolinite duplicate samples produce the same results as the original ones, meaning that they are homogeneous and under the same experiment produce identical results. On the other hand, leaching results for bauxite, red mud waste and laterite samples showed important differences in their leaching results under the same conditions, which is possibly a result of their heterogeneity.

More precisely, comparing both BGS and CSM leaching experiments for Greek bauxite and red mud waste samples, it is obvious that a small amount of REE was removed during the ammonium sulphate leach, even if the BGS leaching results were significantly better. For the M1 S1 sample (which, from XRD, might contain small amounts of kaolinite) the BGS leaching experiment removed 19% of total REE (114 out of 599 ppm) and the CSM leaching experiment removed 3.5% of total REE (21 out of 599 ppm). However, for sample M2 S6 the results were higher with the BGS experiment leaching 47% of total REE (278 out of 594 ppm), while the CSM experiment leached again 3.5% of total REE (20.5 out of 594 ppm). In this context, the CSM test leached 2.9% REE from sample M3 S4 Dupl (14 out of 498 ppm), while for the SQZ S C2 red mud waste sample REE leaching results were almost zero, leaching 00.2% and 0.72% from the duplicate leaching sample (0.21 and 6.31 out of 878.5 ppm, respectively) (Fig. 6.54 and Table 6.11a and b). These results show that samples are heterogeneous, the two experiments have significant differences and that probably there is only a small proportion of REE that are ion adsorbed.

Finally, it is also worth mentioning that from a comparison of the amounts of REE in Greek bauxite and red mud waste samples dissolved into solution during the multi-acid attack used for the ICP-MS trace elements analysis and those leached with ammonium sulphate for the leaching tests at CSM, the multiacid attack dissolved higher amounts of REE. This conclusion is more important

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for red mud samples were multi-acid attack dissolves almost 100% of REE meaning that the residue (if any) does not trap REE. On the other hand, the same protocol BGS tests shows that it can dissolve the same or higher amounts of REE compared to the multi-acid attack, but it is very problematic in leaching HREE (Fig. 6.55).

	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	W	Zr
M1 S1	2.00	60.40	0.30	48.10	13.70	51.80	1.40	11.00	240.20	4.60	51.60	6.20	147.40	513.70
BGS Leaching	0.41	17.06	0.09	0.00	0.01	0.00	0.23	0.00	7.36	0.01	0.29	0.61	0.01	0.06
% Leached	20.72	28.25	31.51	0.00	0.05	0.00	16.65	0.02	3.06	0.13	0.57	9.90	0.01	0.01
CSM Leaching	0.00	3.26	0.09	0.70	0.00	0.02	0.22	0.03	5.14	0.01	0.01	0.02	4.14	0.00
% Leached	0.23	5.39	30.62	1.46	0.02	0.04	15.71	0.31	2.14	0.16	0.01	0.37	2.81	0.00
M2 S6	5.00	41.50	0.10	47.90	15.70	60.80	0.10	14.00	25.00	5.10	66.50	10.50	147.50	573.00
BGS Leaching	0.39	19.20	0.00	0.64	0.03	0.01	0.04	0.01	4.96	0.03	12.68	1.34	0.15	0.64
% Leached	7.86	46.26	0.00	1.33	0.19	0.02	35.44	0.07	19.83	0.51	19.07	12.73	0.10	0.11
CSM Leaching	0.01	4.83	0.01	0.66	0.00	0.02	0.04	0.02	3.42	0.01	0.00	0.04	3.81	0.00
% Leached	0.15	11.63	14.98	1.38	0.01	0.03	38.24	0.16	13.67	0.12	0.01	0.43	2.58	0.00
			-			-				-		-		
M3 S4 Dupl	10.00	143.70	1.00	52.90	13.30	49.40	3.10	11.00	43.50	4.60	45.80	11.10	55.20	500.80
CSM Leaching	0.02	4.08	0.28	0.32	0.00	0.01	0.47	0.01	4.34	0.00	0.00	0.04	3.48	0.00
% Leached	0.18	2.84	27.73	0.61	0.01	0.01	15.15	0.10	9.97	0.09	0.00	0.32	6.30	0.00
SQZ SC2	6.00	53.30	1.70	40.50	30.60	95.40	4.20	21.00	113.20	7.20	95.60	13.50	21.40	1089.50
CSM Leaching	0.00	0.01	0.29	0.00	0.01	0.02	0.73	0.02	16.59	0.01	0.00	0.73	4.72	0.20
% Leached	0.06	0.03	17.22	0.01	0.02	0.02	17.39	0.10	14.65	0.09	0.00	5.41	22.07	0.02
CSM Leaching Dupl	0.03	0.25	0.88	0.13	0.01	0.02	1.15	0.02	26.25	0.01	0.01	0.18	3.96	0.00
% Leached	0.54	0.47	51.58	0.31	0.02	0.03	27.35	0.12	23.19	0.11	0.01	1.30	18.53	0.00

## Table 6.11a. Leaching results for trace elements.

## Table 6.11b. Leaching results for REE.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y	ΣREE+Y
M1 S1	26.70	404.20	13.01	55.80	13.91	3.01	12.88	1.80	9.68	1.85	4.99	0.77	5.18	0.74	44.60	599.12
BGS Leaching	9.31	56.82	5.24	21.09	5.55	1.07	4.19	0.48	2.27	0.34	0.76	0.09	0.45	0.06	6.52	114.25
% Leached	34.88	14.06	40.28	37.80	39.91	35.48	32.55	26.91	23.46	18.44	15.27	11.10	8.67	8.27	14.62	19.07
CSM Leaching	3.24	7.32	1.40	5.63	1.00	0.20	0.78	0.08	0.34	0.05	0.10	0.01	0.04	0.01	1.16	21.37
% Leached	12.12	1.81	10.77	10.09	7.19	6.68	6.05	4.71	3.52	2.77	2.06	1.25	0.80	0.91	2.60	3.57
M2 S6	58.80	384.80	11.68	40.70	7.99	1.74	9.47	1.42	9.16	1.87	5.40	0.86	5.82	0.86	53.20	593.77
BGS Leaching	16.01	221.84	4.25	15.36	3.26	0.61	2.96	0.38	2.18	0.37	0.89	0.10	0.54	0.07	9.50	278.32
% Leached	27.22	57.65	36.41	37.74	40.81	35.31	31.21	27.03	23.84	19.72	16.41	11.87	9.20	7.97	17.86	46.87
CSM Leaching	3.06	12.71	0.57	2.06	0.33	0.07	0.32	0.04	0.19	0.03	0.07	0.01	0.03	0.01	1.08	20.58
% Leached	5.21	3.30	4.89	5.07	4.08	3.88	3.36	2.80	2.06	1.75	1.37	0.87	0.55	0.62	2.03	3.47
M3 S4 Dupl	113.80	146.80	19.20	63.40	14.59	3.64	16.20	3.50	23.29	4.20	12.24	1.93	13.37	2.06	60.10	498.32
CSM Leaching	3.43	3.49	0.68	2.85	0.55	0.14	0.56	0.09	0.50	0.09	0.19	0.02	0.10	0.02	1.63	14.33
% Leached	3.02	2.37	3.53	4.50	3.77	3.79	3.45	2.57	2.14	2.07	1.58	1.09	0.72	0.80	2.71	2.88
SQZ SC2	129.30	421.00	28.27	104.00	20.50	4.40	19.55	3.02	19.86	3.96	11.88	1.95	13.48	2.06	95.20	878.43
CSM Leaching	0.05	0.04	0.01	0.04	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.21
% Leached	0.04	0.01	0.04	0.04	0.04	0.05	0.04	0.05	0.02	0.04	0.03	0.05	0.04	0.08	0.04	0.02
CSM Leaching	1 95	1 27	0.30	1 27	0.19	0.04	0.19	0.02	0.10	0.02	0.06	0.01	0.07	0.02	0.80	6 3 1
Dupl	1.00	1.21	0.00	1.21	0.10	0.04	0.10	0.02	0.10	0.02	0.00	0.01	0.07	0.02	0.00	0.01
% Leached	1.51	0.30	1.08	1.22	0.95	0.99	0.95	0.70	0.50	0.53	0.52	0.51	0.51	0.94	0.84	0.72



Figure 6.55. Chondrite normalized REE diagrams showing the total REE in Greek bauxite and red mud waste samples (ACME), the dissolved REE by multi-acid attack (CSM), the REE leached by using the protocol D at CSM (Leach) and at the BGS (BGS Leach).

To sum up, the BGS test showed that the Sanematsu et al. (2013) protocol is more effective in REE leaching compared to the CSM test, but not as effective in HREE as it is for the LREE. Both CSM and BGS tests show that some amounts of REE occur in bauxites as ion adsorption clays but it seems that protocol D is difficult to apply, as bauxites are heterogeneous and this fact creates problems in stabilizing the solution's pH during the leaching process. Additionally, this protocol does not work at all for red mud waste samples because of their different chemistry and properties and their high pH (approximately 10). As a result it is worth developing this method further or trying another one for REE leaching from bauxites and especially red mud waste.

In this context, the multi-acid attack results indicate that it is worth increasing the amount/concentration of leaching acids and maybe the digestion time. This comes in line with Rao Borra et al. (2015), given that they managed to extract almost 80% of REE from Greek red mud waste samples by using 6 N HCl for 24 h duration at temperature of 25° C with 50:1 liquid-to-solid (L/S) ratio and the REE extraction was increasing with the acid concentration, time and L/S ratio. However, from one point and onwards (critical point) the sample usually becomes saturated, where only slight or no alterations take place even if acid concentration, time or L/S ratio keeps increasing.

Finally, the aforementioned results are promising for further development of the protocol D. On the other hand, the idea of applying a protocol based on the well-accepted BCR technique (CSM protocol), designed to provide a full stepwise REE leaching when required is also interesting. Therefore, a first step involving either magnesium chloride or ammonium sulphate needed to be added in order to extract exchangeable cations without soluble carbonates (Table 5.3). Hence, the pilot test should again include a large range of samples in order to check for the leaching of exchangeable cations. Additionally, for each of the samples there should be a whole rock exchangeable fraction, followed by analysis of the residue by the whole rock technique. This "new CSM protocol" will be tested in the near future.

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# 7. Discussion

## 7.1 Introduction

This chapter describes the mobility of REE in Greek bauxite deposits, discusses their behaviour in comparison to the depth of the mines and presents the REE bearing minerals found in bauxite. Moreover, considering all the data of this thesis and juxtaposing them to the literature, there was made an effort to suggest a model for the behaviour of REE and the formation of the REE bearing minerals in bauxite, as well as a model for the formation of the bauxite itself. Finally, the REE exploitation potential and the feasibility of extraction from red mud waste or directly from bauxite are being discussed.

#### 7.2 REE Mobility in the Bauxite Profiles

Literature review in Chapter 3 indicates that REE are appear to be enriched *per descensum* hitting their maximum concentrations near the bedrock "chemical barrier" and also tend to concentrate in pockets, fissures and cracks in the bauxite. Reports suggest various  $\Sigma$ REE values that range from less than 500 ppm to more than 6,000 ppm (e.g. Valeton et al., 1987; Ochsenkühn-Petropoulou et al., 1994; Laskou and Andreou 2003; Tsirambides and Filippidis, 2012; Eliopoulos et al., 2014; Deady et al., 2014).

This study shows that bauxite's downward REE enrichment does not apply in all deposits of the Parnassus-Giona zone. Bauxite samples gathered from active underground mines (Vargiani, Silas, Gouves and Spartolakka) of B3 horizon show that the  $\Sigma$ REE values in these mines range from 158.7 to 716.3 ppm with the average value to be 369.1 ppm (Table 6.2b). This is in line with Ochsenkühn-Petropoulou et al. (1994) report from blended bauxite samples from Aluminium S.A. that had 560 ppm of  $\Sigma$ REE including Sc and Y and is also in accordance with this study's literature review (also Deady et al., 2014) where the average  $\Sigma$ REE plus Y of B3 horizon are estimated at 417.4 ppm.

Furthermore, it is also very important that the characteristic downward REE enrichment is not present in all mines. This is possibly due to the fact that the mines sampled were active and the sampling positions were not close to the bedrock's chemical barrier. Figures 7.1 to 7.8 show that *per descensum* enrichment is clear in Mine 1 Profile 2, Mine 2 Profile 1 and Mine 4 Profile 1 and

2, whereas in the other profiles downward enrichment is not clear or REE decrease with depth.



Figure 7.1. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 1 of Mine 1 underground B3 bauxite mine.



Figure 7.2. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 2 of Mine 1 underground B3 bauxite mine.



Figure 7.3. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 1 of Mine 2 underground B3 bauxite mine.



Figure 7.4. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 2 of Mine 2 underground B3 bauxite mine.



Figure 7.5. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 1 of Mine 3 underground B3 bauxite mine.



Figure 7.6. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 2 of Mine 3 underground B3 bauxite mine.



Figure 7.7. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 1 of Mine 4 underground B3 bauxite mine.



Figure 7.8. Diagrams showing the REE and  $\Sigma$ REE values in comparison with depth in the Profile 2 of Mine 4 underground B3 bauxite mine.

It is also evident that Ce, as the predominant element, controls the  $\Sigma$ REE+Y behavior. In most of the profiles  $\Sigma$ REE generally follows cerium's trend, apart from Mine 2 Profile 1 and Mine 3 Profile 1, where lanthanum appears in high concentrations at specific positions. However, each REE solely appears to follow the trend of lanthanum or neodymium for instance, and not cerium's trend. Yttrium does not seem to follow cerium's trend as well. This does not happen at Mine 1 Profile 1, where all REE follow the same trend.

Figures 7.9 to 7.16 clearly show that light REE excluding cerium and heavy rare earths including yttrium follow the enrichment trends lanthanum or neodymium. Furthermore, it seems that HREE do not show any significant enrichment downwards, but their values rather stay constant or occasionally slightly increase. The same happens for LREE without the huge impact of cerium and occasionally lanthanum and neodymium effect.



Figure 7.9. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 1 Profile 1.



Figure 7.10. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 1 Profile 2.



Figure 7.11. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 2 Profile 1.



Figure 7.12. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 2 Profile 2.



Figure 7.13. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 3 Profile 1.



Figure 7.14. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 3 Profile 2.



Figure 7.15. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 4 Profile 1.



Figure 7.16. Diagrams of REE values, Ce/Ce\* and Eu/Eu\* anomalies compared to depth at bauxite Mine 4 Profile 2.

Finally, other trace elements such as the HFSE, LILE and transition metals do not appear to be enriched or depleted with depth (Fig. 10.38 to 10.45). However, mobile trace elements such as Rb, Sr, Ba, Ni and Cr display a downward enrichment in *in situ* bauxitized karst deposits (Maksimović et al., 1991; Mongelli, 1997) in the same way REE are getting concentrated in the lowermost parts of the deposit (Maksimović and Pantó, 1996). The fact that these elements are not getting enriched downwards strengthens the argument that this study's sampling profiles are not close to the limestone bedrock.



Figure 7.17. Chondrite normalized REE patterns for bauxite samples from Mine 1 using McDonough and Sun (1995).



Figure 7.18. Chondrite normalized REE patterns for bauxite samples from Mine 2 using McDonough and Sun (1995).



Figure 7.19. Chondrite normalized REE patterns for bauxite samples from Mine 3 using McDonough and Sun (1995).



Figure 7.20. Chondrite normalized REE patterns for bauxite samples from Mine 4 using McDonough and Sun (1995).



Figure 7.21. Average chondrite normalized REE patterns for each bauxite profile using McDonough and Sun (1995).



Figure 7.22. Average chondrite normalized REE patterns for each bauxite mine using McDonough and Sun (1995).



Figure 7.23. Average chondrite normalized REE patterns for the 3<sup>rd</sup> bauxite horizon using McDonough and Sun (1995).

Average total REE values do not show significant variations between different profiles or different mines (Table 7.1 and Fig. 7.21, 7.22 and 7.23). Mine 1 has the lowest REE concentrations (316.6 ppm) as its 1<sup>st</sup> profile sampled has 286.1 ppm  $\Sigma$ REE+Y. Mine 3 has the highest REE content (417 ppm) as M3 P1 has 484.7  $\Sigma$ REE+Y content respectively. Chondrite normalized patterns using McDonough and Sun (1995) are similar for almost all samples with positive Ce and negative Eu anomaly, apart from samples M2 S5 and M3 S4 where there is negative Ce anomaly (Fig. 7.17, 7.18, 7.19 and 7.20). The Ce/Ce<sup>\*</sup> index ranges from 0.7 to 13.5 and its average is 5.3, whereas the Eu/Eu<sup>\*</sup> index ranges from 0.6 to 0.7 respectively (Table 6.2b).

Table 7.1. Average  $\Sigma REE$  (ppm) values of each profile, each mine and of the B3 horizon.

M1 P1	M1 P2	M2 P1	M2 P2	M3 P2	M3 P1	M4 P2	M4 P1				
286.1	347.1	324.2 478.5		332.5 484.7		365.8	305.7				
Min	ne 1	Min	ne 2	Min	ne 3	Mine 4					
316.6		40	1.3	41	7.1	335.8					
3 <sup>rd</sup> Bauxite Horizon											
369.1											

Percolating pore water controls the mobility of REE as LREE are leached under acidic conditions and HREE under alkaline or weakly alkaline conditions. La/Y ratio (in absolute values) defines the deposition environment (<1 for acid and >1 for alkaline) (Crnicki and Jurkovic, 1990) and the highest La/Y ratios occur near the bedrock of the deposits (Maksimović et al., 1991). Additionally, La/Lu, La/Y and  $\Sigma$ LREE/ $\Sigma$ HREE ratios tend to have their highest values in the lower parts of the deposits, which indicates that these bauxite deposits were multistage reworked and enriched (Laskou and Andreou, 2003).



Figure 7.24. Diagrams showing the  $\Sigma LREE/\Sigma LREE$ , La/Y and La/Lu ratios with depth at the underground bauxite Mine 1.



Figure 7.25. Diagrams showing the  $\Sigma LREE/\Sigma LREE$ , La/Y and La/Lu ratios with depth at the underground bauxite Mine 2.



Figure 7.26. Diagrams showing the  $\Sigma LREE / \Sigma LREE$ , La/Y and La/Lu ratios with depth at the underground bauxite Mine 3.



Figure 7.27. Diagrams showing the  $\Sigma LREE/\Sigma LREE$ , La/Y and La/Lu ratios with depth at the underground bauxite Mine 4.

La/Y ratios in absolute values (not chondrite normalized) in this study's bauxite deposits ranges from 0.2 to 3.5 but in the vast majority of samples are below 1, indicating an acidic deposition environment (Table 6.2b and Fig. 7.24 to 7.27) that occasionally changes into alkaline. Samples M2 S5 and M3 S4 that showed negative Ce anomaly also have higher than 1 La/Y ratio (3.5 and 1.9 respectively). The alkaline environmental conditions in these two specific positions explain relatively low Ce values in contrast to the high concentrations

of the rest rare earth elements. Moreover, La/Lu, La/Y and  $\Sigma$ LREE/ $\Sigma$ HREE ratios at Figures 7.24, 7.25 and 7.27 show that *per descensum* enrichment occurs again only at Mine 1 Profile 2, Mine 2 Profile 1 and Mine 4 Profile 1 and 2 and it is in line with Figures 7.10, 7.11, 7.15 and 7.16. More precisely, La/Y and  $\Sigma$ LREE/ $\Sigma$ HREE ratios do not show significant variations, whereas La/Lu ratio shows important variations mainly controlled by fluctuations in the concentrations of lanthanum (Table 6.2b). Furthermore, there are cases where  $\Sigma$ LREE/ $\Sigma$ HREE ratio slightly decreases downwards indicating an enrichment of HREE relative to LREE.

Cerium's behavior, which does not follow that of the other REE (does not increase downwards), has been reported in karst bauxite deposits of both Greece and Italy (Maksimović and Pantó, 1996; Mongelli, 1997; Laskou and Andreou, 2003; Mameli et al., 2007; Mondillo et al., 2011; Boni et al., 2013; Mongelli et al., 2014). This is caused by the oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup> in a strongly oxidising environment during bauxitization (Maksimović and Roaldset, 1976; Koicki et al., 1980; Maksimović et al., 1993). As a result Ce is enriched in the upper parts of the bauxite deposit while other REE are being washed downwards. This is also in line with studies on coal layers overlying the Greek bauxite deposits, which demonstrate positive Ce anomaly due to intense weathering (Worrall and Pearson, 2001; Kalaitzidis et al., 2010).

# 7.3 REE Mineralogy of Bauxites and Comparison with Other Localities

REE bearing minerals in bauxite are divided into detrital and authigenic. Laskou and Andreou (2003) first reported the occurrence of detrital REE bearing phosphate minerals in Greek bauxite such as rhabdophane-Ce, florencite-Ce, churchite and xenotime. On the other hand, monazite and other fluorocarbonate bastnäsite/parisite-group minerals such as hydroxylbastnäsite are the authigenic ones (Maksimović and Pantó, 1996; Lymperopoulou, 1996; Gamaletsos et al., 2011).

This study first reports that monazite appears as a detrital REE mineral, while detrital zoned zircons may possibly be the source of scandium in the Parnassus-Giona bauxite. Additionally, the predominant very high Ce and Ca containing authigenic minerals are not fluorocarbonates or phosphates, given that SEM and EPMA analyses showed the absence of fluorine and phosphorus. Hence, these minerals are more likely to be Ce oxides or carbonates and not hydroxylbastnäsites (with all their F completely substituted by OH) because other REE apart from Ce are absent or almost absent.

This study also demonstrates that very small amounts of REE in bauxites occur as ion adsorption clays. Kaolinite occurs locally by forming mixtures with AI hydroxides. Alteration of bauxite grains and matrix is caused kaolinization at a LP/LT (low pressure and low temperature) system. More precisely, kaolinization (Si metasomatism and potential AI remobilization) is possibly triggered because of the downward flow of siliceous water through pores, cracks and fissures in bauxite during the epigenetic stage (Dangić, 1988).

More precisely, in Parnassus-Giona bauxites there are reported occurrences of LREE fluorocarbonate bastnäsite/parisite-group minerals and secondary Ca containing hydroxylbastnäsites (Lymperopoulou, 1996: Gamaletsos et al., 2011). On the other hand, reports from Italy indicate the presence of supergene LREE enriched high Ce, low La-Nd also containing Ca phosphates derived from the weathering of monazite in Southern Apennines bauxite (Mondillo et al., 2011; Boni et al., 2013). Additionally, Apulian (southern Italy) bauxites contain authigenic high Ce, Ca containing fluorocarbonate minerals of the bastnäsite group (Mongelli, 1997; Mongelli et al., 2014). Although Nurra (Sardinia) bauxite studies (Mameli et al., 2007) refer to the presence of REE minerals possibly of the bastnäsite group, SEM/EDS analysis showed that these minerals contain high Ce and Ca but no F. This last report is in agreement with the present study and confirms the occurrence of the same authigenic REE minerals in Greek bauxite, which can be related to the anomalous enrichment of cerium. This study's authigenic REE minerals cannot belong to the bastnäsite group even if they are hydroxylbastnäsites with their F content totally been replaced by OH. This is because there are no other REE apart from Ce present in the crystals.

# 7.4 Model for REE in Bauxite

The identification of parisite in addition to the Ce anomaly fluctuation throughout the whole bauxite deposit at Spinazzola (Apulia, southern Italy), not only near the carbonate bedrock, led to the suggestion of the following genetic model (Mongelli, 1997; Mongelli et al., 2014):

- 1) Cerianite solubilization via cerium reduction.
- 2) Cerium transportation per descensum.
- 3) Parisite precipitation.

This model works assuming that ubiquitous cerianite is present in the original bauxite similarly occurring in laterites (Braun et al., 1990) and iron-rich soils (Deng et al., 2010). The cerianite dissolution and parisite precipitation cycle can be repeated several times as cerium's remobilization needs acidic conditions or low Eh, whereas the precipitation of parisite requires alkaline conditions. Both can be achieved at an alkaline environment where Eh fluctuates cyclically. Fluctuations of the groundwater level may contribute to the dissolution of cerianite (Ce/Ce\* $\leq$ 1) and the precipitation of parasite (Ce/Ce\* $\geq$ 2).

This model might work for Greek bauxites as well. Results of the current study based on the La/Y ratios show that the deposition environment is acidic apart from samples M2 S5 and M3 S4 (La/Y ratio is 3.5 and 0.8 respectively) where it is clearly alkaline. These samples are also the only ones that have Ce/Ce\* values below one (0.8 for M2 S5 and 0.7 for M3 S4) (Fig. 7.3 to 7.6 and Table 6.2b). This may suggest that Ca containing cerianite occurs in crystalline form in almost all samples, whereas in specific positions like M2 S5 and M3 S4 different authigenic minerals may occur/crystallize as the deposition environment changes. Additionally, cerium's oxidation from Ce<sup>3+</sup> to Ce<sup>4+</sup> generally causes a strong decrease in the elemental mobility and the precipitation of Ce-oxidized minerals (Mongelli, 1997). This explains the predominant presence of Ce in all parts of the Greek bauxite deposits sampled, in addition to the positive Ce anomalies, the anomalous Ce enrichment and the insignificant downward REE enrichment observed. Consequently, the bauxite mines sampled are possibly very deep and the samples collected belong to higher parts of the bauxite profiles where Ce oxidation usually takes place.

All these features characterize REE in Parnassus-Giona bauxite along with the presence of detrital monazites and Sc and Hf bearing zircons (in the Italian bauxite zircons also contain Ca). If monazites were more abundant, their weathering could lead to the formation of secondary authigenic high Ce, Ca containing phosphates (Mondillo et al., 2011; Boni et al., 2013). This study's authigenic REE minerals do not contain F or P, thus they are not phosphates or fluorocarbonates. The lack of P and F means that Ce remobilization cannot occur via phosphate or fluoride complexes. It has possibly washed downwards as oxides or calcium carbonate complexes under acidic conditions, filling pores and cracks, until it finds alkaline conditions or is stopped by the alkaline barrier of the limestone bedrock.

Although the present study does not include XRF quantitative Fe data, neither Fe<sub>2</sub>O<sub>3</sub> content or bauxite color seem to correlate positively or negatively with  $\Sigma REE$  content. That is because high  $\Sigma REE$  concentrations occur at both hematite-goethite rich (red) and poor (yellow) samples. In the same context, the presence of boehmite or diaspore does not correlated somehow with the  $\Sigma REE$ content. This is in contrast to other studies on REE in Greek bauxites, which claim that Fe<sub>2</sub>O<sub>3</sub> is negatively correlated with REE content and positively correlated LREE/HREE ratio (Laskou and Andreou, 2003; Gamaletsos et al., 2011; Eliopoulos et al., 2014). Moreover, studies at the Italian karst bauxites indicate that Fe-minerals are controlling the distribution of REE and La content depends on Fe content (Mongelli, 1997). REE and especially LREE tend to concentrate in Fe-rich bauxite horizons, as a slightly positive correlation exists between  $Fe_2O_3$  and  $\Sigma REE$  probably because of the scavenging by goethite (Mameli et al., 2007). However, it is also noted that very high REE contents occur in a Fe-depleted horizon as a result of the presence of REE minerals, probably of the bastnäsite group.

# 7.5 Model for the Formation of Bauxite

Concisely, the Greek allochthonous bauxite deposits of Central Greece were formed by loose lateritic material that originated from serpentinites as well as metamorphic and magmatic rocks. This material was transported from an emerging terrestrial hinterland that underwent lateritic weathering to a brackish marine or lagoonal environment. Transportation was carried out via a branching river network of NE to SW direction (Papastamatiou, 1960; Bárdossy and Mack, 1967; Nia, 1968; Valeton et al., 1987). The conveyed material flowed over a karstified carbon platform in the form of colloidal solutions and trapped in karst depressions of the calcareous rock.

A unique characteristic of the Parnassus-Giona bauxite is its high Ni-Cr contents that indicate an ophiolitic origin, whereas other karst bauxite deposits have significantly lower Ni-Cr contents, which means that their parent material is unrelated to ophiolites (Öztürk et al., 2002; Laskou and EconomouEliopoulos, 2007; Mameli et al., 2007; Kalaitzidis et al., 2010; Mondillo et al., 2011). The 2,000 to 3,000 ppm average concentrations of Ni and Cr in Greek bauxites indicate probably a contribution from ultramafic rocks during weathering (Aronis, 1955; Maksimović and Papastamatiou, 1973; Combes, 1979). Özlü (1983) also linked Parnassus-Giona karst bauxites of the 3<sup>rd</sup> horizon to ultramafics as their parent rocks by using Cr, Ga and Zr contents. Finally, Valeton et al. (1987) suggested that bauxites and Fe-Ni laterites of Central Greece originate from serpentinites as well as from metamorphic and magmatic rocks occurring at Euboea and Lokris areas (Fig. 7.28 and 7.29).







Figure 7.29. Simplified geotectonic map of the Dinarides-Hellenides orogenic belt showing the main tectono-stratigraphic units and ophiolite, laterite and bauxite occurrences (modified from Robertson and Shallo, 2000 and Barth et al., 2008).
Table 7.2. Average Eu anomaly of various potential parent or bauxite related

#### rocks.

Location	Rock Type	Eu/Eu* Ratio	Reference
Pindos Ophiolites	Epidosite	1.2	Valsami and Cann (1992)
Pindos Ophiolites	Albite Epidosite	0.9	Valsami and Cann (1992)
Pindos Ophiolites	Basalt	0.9	Valsami and Cann (1992)
Pindos Ophiolites	Stockwork	0.7	Valsami and Cann (1992)
Pindos Ophiolites	Harzburgite Upper Unit-Mantle Sequence	1.8	Saccani and Photiades (2004)
Pindos Ophiolites	Basalt Lower Unit-Lower Pillow Sequence	0.9	Saccani and Photiades (2004)
Pindos Ophiolites	Basaltic Andesite Lower Unit-Massive Lavas	0.8	Saccani and Photiades (2004)
Pindos Ophiolites	Basaltic Andesite Lower Unit-Upper Pillow Sequence	0.9	Saccani and Photiades (2004)
Pindos Ophiolites	Basalt Lower Unit-Dykes	1.0	Saccani and Photiades (2004)
Pindos Ophiolites	Basaltic Andesite Lower Unit-Dykes	1.0	Saccani and Photiades (2004)
Othris Ophiolites	Rodingite	2.1	Tsikouras et al. (2009)
Othris Ophiolites	Dolerite	1.1	Tsikouras et al. (2009)
Othris Ophiolites	Plagioclase Peridotite	1.0	Barth et al. (2008)
Othris Ophiolites	Lherzolite	1.0	Barth et al. (2008)
Othris Ophiolites	Harzburgite	1.2	Barth et al. (2008)
Othris Ophiolites	Dunite	1.4	Barth et al. (2008)
Othris Ophiolites	Ultramylonite	1.4	Barth et al. (2008)
Iti Ophiolites	Rodingite	1.5	Tsikouras et al. (2013)
Iti Ophiolites	Harzburgite	1.2	Tsikouras et al. (2013)
Iti Ophiolites	Lherzolite	0.6	Tsikouras et al. (2013)
Iti Ophiolites	Gabbro	1.5	Tsikouras et al. (2013)
Kallidromon Ophiolites	Rodingite	1.5	Tsikouras et al. (2013)
Kallidromon Ophiolites	Dolerite	1.5	Tsikouras et al. (2013)
Euboea Amphibolites	Amphibolite	1.1	Gartzos et al. (2009)
Marmeiko Laterites	Nickeliferous Iron Ore	0.7	Skarpelis et al. (1989)
Marmeiko Laterites	Ferruginous Clays	0.7	Skarpelis et al. (1989)

The Eu/Eu\* ratio seems to remain unchanged during intense weathering (Mameli et al., 2007). Eu/Eu\* ratio in the current study is rather constant between 0.6 and 0.7 (Fig. 7.9 to 7.16 and Table 6.2b) and it is very close to the average value of 0.66 for Upper Continental Crust (UCC) (Taylor and McLennan, 1985). The average Eu anomaly of various potential bauxite protoliths from the literature ranges between 0.6 and 2.1. Similar to bauxite average Eu anomaly values found in the Pindos ophiolite stockwork, in the Iti Lherzolite and in REE rich laterites of the Marmeiko deposit (Table 7.2).

The REE patterns of the potential protoliths of the bauxites from the literature were also checked to identify if the characteristic negative Eu anomaly and positive Ce anomaly (which is a result of the presence of high Ce minerals in bauxite) are present. However, REE patterns for the protoliths showed a poor fit to that of the bauxite (Fig. 7.30 to 7.33). REE patterns coming from literature data show that plagioclase peridotite 2 and harzburgite 7 and 9 of Othris ophiolite (Fig. 10.47 and 10.48) show a slight positive Ce anomaly but they do not have negative Eu anomaly and their HREE are quite enriched. On the other hand, Iti gabbro REE pattern (Fig. 10.49) seems to be similar to the bauxite

REE pattern. In terms of distance, the Iti and Kallidromon ophiolites are closer to the bauxites and hence it is more likely that they are genetically linked, whereas the Pindos and Othris ophiolites are relatively far. Moreover, from the literature it is more likely that the bauxites are associated with ophiolites and ultramafic rocks in the Lokris and Euboea areas (Valeton et al., 1987; Petrascheck, 1989; Valeton, 1994), as well as the Iti and Kallidromon ophiolites that are located close to the area where bauxites occur.



Figure 7.30. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Pindos ophiolites (bauxite potential parent rocks).



Figure 7.31. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Othris ophiolites (bauxite potential parent rocks).



Figure 7.32. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Iti and Kallidromon ophiolites (bauxite potential parent rocks).



Figure 7.33. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Euboea amphibolites (bauxite potential parent rocks).

In this context, Eu anomalies in the Marmeiko laterite deposit, which is also located in the Lokris area, show it is genetically related to the Parnassus-Giona bauxite deposits even if those two different deposits do not share similar REE patterns (Table 7.2, Fig. 7.34 and 10.51). This is in line with the literature as the Marmeiko laterite deposit belongs to the karst type deposits having a Jurassic limestone as bedrock, it is covered by an Upper Cretaceous limestone and it was formed by the weathering of ophiolites (Skarpelis et al., 1989). Therefore, it is not by coincidence that the Marmeiko and Parnassus-Giona deposits have the same Eu/Eu\* ratios, given that bauxites are supposed to be formed by the reworking and transportation of laterites, which were formed by the weathering of ophiolites and ultramafic rocks of Central Greece. On the other hand the different REE patterns and concentrations can be explained by the different local weathering conditions. More precisely, the Marmeiko deposit contains 1,752 ppm of  $\Sigma$ REE on average (ranges from 1,288 to 2,452 ppm) in nickeliferous iron ore and 413 ppm of SREE on average (ranges from 375 to 517 ppm) in ferruginous clays (Skarpelis et al., 1989). This deposit was formed by material originating from the weathering of ultramafic rocks rich in iron, nickel and chromium and silicate REE rich rocks, while hydroxylbastnäsite-Nd is the predominant authigenic REE mineral (Maksimović and Pantó, 1996).



Figure 7.34. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Marmeiko laterite deposit.

Finally, REE patterns, Eu anomalies and Ni-Cr contents are very useful tools for associating bauxites to their parent rocks. However, given that these rocks are so heterogeneous, more extensive REE datasets are needed for that kind of research. In this context, isotope studies and dating of detrital minerals such as zircons would be extremely helpful for further and more accurate identification of the bauxite protolith. In conclusion, it is worth mentioning that only a combination of all of the aforementioned methods could result in a detailed genetic model for the bauxites, as apart from its very complex formation processes, bauxite is likely to originate from a mixture of parental materials from rocks located in different areas of Central Greece.

### 7.6 Potential of REE Exploitation from Bauxite and Red Mud Waste

Red muds are produced at a rate of approximately 150 Mt per year globally. There are now approximately 60 alumina refineries worldwide outside China using the Bayer process, of which 10 are located in Europe (Fig. 7.35). An additional 49 refineries were operating in China in 2011 (IAI, 2014). Some of refineries produce very REE enriched red muds, like the Jamaican ones that contain 0.23-0.38 wt.% REE for instance (Mariano and Mariano, 2012). European refineries produce alumina from both European and imported bauxite in order to supply the needs of the European market. The importation of bauxite from a wide range of sources makes it difficult to assess the REE content of the resulting red mud waste. In Europe, the largest alumina refinery is Aughinish in the Republic of Ireland, which has an output of 1.93 Mt of alumina per annum. Each tonne of alumina produced results in the formation of between 0.7 and 2 tonnes of red mud (IAI, 2014). Assuming an average overall ratio of 1:1.5 alumina to red mud (Hamada, 1986; Power et al., 2011), the Aughinish plant is likely to produce almost 3 Mt of red mud per annum.

Worldwide, an estimated 2.7 billion tonnes (Bt) of red muds have been produced since the development of the Bayer process (Power et al., 2011). These have been treated in a variety of ways, including storage in onshore lagoons and direct marine 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).



Figure 7.35. World map showing the distribution of alumina refineries based on establishment date (before or after 1970), closed or unknown (Power et al., 2011).

Production of REE in the form of RE oxides (REO) is currently limited to six countries: Russia, USA, China, Brazil, Malaysia and Australia (Brown et al., 2014). Bauxite mining companies in Greece extracted 2.3, 1.8 and 2.0 Mt of bauxite during 2011, 2012 and 2013, respectively (Tsirambides and Filippidis, 2012; Brown et al., 2014; Lee-Bray, 2014). This means that the average extraction of bauxite is approximately 2.0 Mt per annum out of the 100 Mt estimated bauxite reserves (O'Driscoll, 2011). Aluminium S.A. is the largest bauxite consumer in Greece processing more than 1.5 Mt/year. Today, Aluminium S.A. produces about 810,000 t of alumina annually, from which 490,000 t are exported and 320,000 are used for aluminium production. These produce approximately 165,000 t of aluminum, from which 100,000 t are again exported, while the remaining 65,000 t are sold in the Greek market.

Production of red muds can vary from 0.3 to as high as 2.5 t of residue per t of alumina produced, though typically it lies between 0.7 and 2 t of residue per t of alumina produced. Currently red mud in Greece is produced at almost 1:1 mass ratio to metallurgical alumina. Therefore, Aluminium S.A. is producing approximately 700,000 t of red mud waste by processing about 1.5 Mt of bauxite per year (Anagnostou, 2010). Additionally, dehydrated red mud deposition near the Aluminium S.A. plant has started in 2009. Hence, REE bearing red mud waste stockpiles are estimated approximately 4.2 Mt at the end of 2014.

This study shows that average  $\Sigma REE$  in bauxite is 327.7 ppm and 769.3 ppm in red mud waste, while the enrichment factor is 2.3. Additionally, the  $\Sigma REE$  content including Y in bauxite is 369.1 ppm and in red mud waste is 867.5 ppm, with 2.4 enrichment factor (Fig. 7.36). However, bauxite's average realistic  $\Sigma REE$  content including Sc and Y according to the literature is roughly 500 ppm and 1000 ppm for red mud waste, while the average enrichment factor is about 2.0. At this point it should also be mentioned that there are specific mines or positions in the mines where REE concentrations appear to be significantly higher than the average of 500 ppm.





Considering all the aforementioned data, 100 Mt of bauxite reserves can contain from 36,910 to 50,000 t of REE in total, assuming an REE range between 369.1 and 500 ppm. In the same context, 4.2 Mt of dehydrated red mud waste stockpiles may contain from 3,643.5 to 4,200 t of REE, assuming that REE vary from 867.5 to 1000 ppm. Moreover, Aluminium S.A. processes annually about 1.5 Mt of bauxite that contains 553.65 to 750 t of REE, whilst the Bayer process produces approximately 700,000 t of red mud waste per year, which contains from 607.25 to 700 t of REE.

Whether REE are extracted from the Bayer Process or leached directly from bauxite they are 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. It is notable that the data also show a relatively high content of LREE relative to HREE, which may have economic implications. However, there are challenges associated with the exploitation of red mud waste and more specifically with 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 (Deady et al., 2014).

Fully understanding the mineralogy and natural processes of REE enrichment in bauxites is vital for assessing the REE resource potential of bauxites and red muds in Greece and Europe in general. Great variability in both the mineral concentration and composition between and along bauxite horizons is documented (Maksimović and Pantó, 1996). This means acquiring red muds with consistent REE concentrations to feed a processing plant would be challenging. 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 (Wall, 2014). 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 potential REE resource rather than a waste product with the associated disposal issues.

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Undoubtedly, the quantities of REE contained in red muds appear to be low (1000 ppm on average including Sc and Y) when compared with primary deposits of carbonatite such as Mountain Pass and Mount Weld, which have grades of about 80,000 ppm REE (Wall, 2014). However, REE from Greek annual bauxite or red mud production could approximately account for the 2.5 percent of EU annual demand, given that EU imports of rare earths in 2011 (REE plus Sc and Y metals and compounds) totaled about 26,500 t (Brown et al., 2013).

More significantly, availability of REE derived from Greek bauxites and/or red muds may contribute to improving the security of supply for some REE to the European market. European production of would ensure a secure supply source and remove some of the risks associated with the importation of REE from geopolitically unstable countries (Deady et al., 2014). The economic viability of REE production from Greek and European bauxites and red muds needs careful assessment due to the investment required in mineral processing and extraction technology. Further research, focused on improved characterization 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.

### 7.7 REE Extraction from Bauxite and Red Mud Waste

Although Ce is the least valuable of the REE, it is the most abundant REE in Greek bauxite and red mud waste. Ce average concentration is approximately 230 ppm in bauxite and 411.3 ppm in red mud, whereas the concentration of the remaining REE is about 139.1 ppm in bauxite and 456.2 ppm in red muds (Fig. 7.37). Consequently, even if Ce might not be worth leaching, the approximately 500 ppm of the remaining REE in red mud waste could be an important alternative REE source. Various researchers (e.g. Lymperopoulou, 1996; Ochsenkühn-Petropoulou et al., 1996; Ochsenkühn-Petropoulou et al., 2002; Rao Borra et al., 2015) showed that REE could be leached from red mud by using strong acids. However, it is undoubtedly needed further development of a method that could leach the 100% of REE contained in bauxite in order to produce an economic REE product.



Figure 7.37. Ce and  $\Sigma$ REE-Ce concentrations (ppm) in bauxite and red mud waste.

As far as REE leaching directly from bauxite is concerned, the 139.1 ppm of REE (excluding Ce) in bauxite is not currently worth leaching. However, analyzed bauxite samples in the current study show that Ce concentration is higher compared to the Greek bauxite average, as the enrichment factor for Ce is 1.8 (Table 5.6). This is due to the fact that these samples are possibly located in the upper parts of the bauxite profile where Ce occurs in the form of cerianite or it is dissolved and precipitated (Section 7.2 and 7.4). This argument is also in line with the leaching results of Section 5.5.2, which shows that bauxite contains an amount of REE in the form of ion adsorption clays. Hence, if the aim is the REE leaching from bauxite, Ce concentration is a very useful tool to identify from which part of the bauxite profile the mined ore is coming from. Ce rich samples could be used as indicators in order to locate and leach REE out of bauxite that is mined from deeper parts of the deposit.

Finally, regarding the direct REE leaching from bauxite, it is particularly important to know from which part of the profile bauxite is mined because of the difference in REE minerals and concentrations. Apart from detrital REE minerals, different authigenic REE minerals occur in various parts of a bauxite profile:

- 1) Upper parts of bauxite profile: Contains high amounts of Ce that occur in ion adsorption clays or in the form of cerianite.
- Middle parts of bauxite profile: Contains REE, especially LREE, which tend to be concentrated in Fe-rich bauxite layers probably because of scavenging by iron oxides from Ce-depleted percolating solutions.
- 3) Lower parts of bauxite profile: Contains REE minerals consisting usually of La, Nd and HREE. F can be substituted by -OH groups resulting to the formation of hydroxylbastnäsite. Additionally, parisite can be formed as a result of precipitation of Ce<sup>3+</sup> as a fluorocarbonate or carbonate-fluoride complex.

Consequently, the precipitation of REE seriously affects REE leaching from bauxite, which could be feasible only from bauxite mined from the middle and even better from the lowermost parts of the deposit. Additionally, the remobilization of REE might also affect the red mud waste stockpiles. Therefore, if red muds are stockpiled and weathered over long time periods, REE could precipitate and enrich the base of the stockpiles, which could be used for REE leaching. Moreover, if the leachates contain high amounts of REE, there could be developed a method to collect them.

In terms of feasible and viable REE exploitation it is obvious that the upper part of the bauxite deposit has to be separated from the remaining bauxite profile during mining and should be leached with a method that targets the extraction of ion adsorption clays to extract Ce if it can be an economic product. The middle and lower parts of bauxite should be mined and deposited in a different area and leached with acids for Nd and HREE. In this scenario, a by-product extraction plant could be placed exactly before the Bayer process and consequently the new red mud waste produced will be REE depleted and won't need re-mining. As far as the REE enriched red mud stockpiles are concerned, they could be left as an REE back up emergency source. Additionally, if REE are transported downwards, a very REE enriched deposit could be formed at the bottom of the stockpiles that could be worth leaching. However, if REE leaching from red muds costs less than from bauxites or achieves higher recovery rates, the idea of selective mining and REE leaching from bauxite should be abandoned. The Bayer process should remain as it is and leaching applied to red muds only.

# 8. Conclusions - Suggestions

### **Conclusions on the Mobility of REE:**

- Downward REE enrichment in the bauxites does not occur in all mines, but only at Mine 1 Profile 2, Mine 2 Profile 1 and Mine 4 Profile 1 and 2.
- Ce concentrations in bauxite samples from the current study are higher compared with the average for Greek bauxites, with an enrichment factor of 1.8. These samples come from the upper parts of the bauxite profile where Ce occurs in the form of cerianite or adsorbed onto clays.
- Ce is the predominant REE in the bauxites and controls the ΣREE enrichment, while each of the remaining REE follows the enrichment trend of lanthanum or neodymium for instance.
- The behavior of Ce in the bauxites is largely controlled by the oxidation of Ce<sup>3+</sup> to Ce<sup>4+</sup> in a strongly oxidizing environment during bauxitization. Ce is enriched in the upper parts of the bauxite deposit while other REE are being washed downwards.
- Chondrite normalized patterns for the bauxites are slightly LREEenriched. Most of the samples have a characteristic positive Ce and negative Eu anomaly.
- The Ce/Ce\* index for the bauxites ranges from 0.7 to 13.5 and its average is 5.3, whereas the Eu/Eu\* index ranges from 0.6 to 0.7.
- HREE do not show any significant enrichment downwards in the bauxites, whereas LREE are enriched downwards due to the high concentrations of Ce and occasionally of La and Nd.
- La/Lu ratio shows important variations mainly controlled by fluctuations in the concentrations of lanthanum.
- La/Y ratio in absolute values ranges from 0.2 to 3.5 but in the vast majority of bauxite samples it is below 1. This indicates an acidic deposition environment that occasionally changes into alkaline.
- The Fe<sub>2</sub>O<sub>3</sub> content, the color of bauxite and the presence of boehmite or diaspore do not correlate positively or negatively with the ΣREE content.

### Conclusions on the REE Mineralogy of Bauxite:

- The predominant very high Ce and Ca containing authigenic REE minerals in the bauxites are not fluorocarbonates, phosphates or hydroxylbastnäsites but are more likely to be cerianite.
- The Ca containing cerianite occurs in crystalline form in almost all samples that are from acidic conditions apart from samples M2 S5 and M3 S4, where different authigenic minerals might occur due to their alkaline environment.
- Bauxite samples M2 S5 and M3 S4 also show a negative Ce anomaly and have higher than 1 La/Y ratio. Those samples occur in an alkaline environment that explains the relatively low Ce values in contrast to the high concentrations of the rest rare earth elements.
- Monazite occurs as a detrital REE mineral.
- Zircon occurs in three types: Sc-bearing also containing Th, Hf-bearing and pure zircon.
- From leaching tests small amounts of REE occur as adsorbed ions, probably adsorbed to the surfaces of clays. Kaolinite occurs locally in mixtures with Al hydroxides. REE minerals tend to concentrate in or near kaolinized grains as well as in cracks, veins and fissures in the bauxite.

### **Conclusions on the Potential Protoliths of Bauxite:**

- The Eu/Eu\* ratio (0.6 and 0.7) remains unchanged during intense weathering. Eu/Eu\* values similar to bauxite are found in ophiolite stockworks on the Pindos mountain, Iherzolites in the Iti mountain and in REE rich laterites of the Marmeiko deposit, making these potential parent rocks. In addition, the REE pattern of gabbro from Iti mountain appears to be similar to that of the bauxites.
- Eu anomalies in the Marmeiko laterite deposit (Lokris area) show it is genetically related to the Parnassus-Giona bauxite deposits even if those two different deposits do not share similar REE patterns. This is because bauxites were formed by the reworking and transportation of laterites, which were formed by the weathering of ophiolites and ultramafic rocks of Central Greece.

 The different REE patterns, REE concentrations and authigenic REE minerals in laterites and bauxites can be due to various factors. These may include differences in local weathering conditions, in geomprphological conditions, in the speed of lateritization/bauxitization or in the proportion of the mixed parental material coming from the weathering of different protoliths.

# Conclusions on the REE Exploitation Potential From Greek Bauxite And Red Mud Waste:

- Bauxite from Vargiani, Silas, Gouves and Spartolakka active underground mines of the B3 horizon contains ΣREE from 158.7 to 716.3 ppm, with an average of 369.1 ppm.
- 100 Mt of bauxite reserves in Central Greece contain from 36,910 to 50,000 t of REE in total, assuming a total REE range of 369.1 to 500 ppm.
- 4.2 Mt of dehydrated red mud waste stockpiles may contain from 3,643 to 4,200 t of REE, assuming that REE vary from 867.5 to 1000 ppm.
- 1.5 Mt of bauxite processed annually by Aluminium S.A. contains 553 to 750 t of REE.
- 700,000 t of red mud waste produced through Bayer process per year contains from 607.25 to 700 t of REE.

## Conclusions on the REE Leaching Tests

- The Sanematsu et al. (2013) protocol proved that some amounts of REE occur in bauxites as ion adsorption type deposits.
- The Sanematsu et al. (2013) protocol does not work at all for red mud waste samples because of their different chemistry and properties and their high pH.
- Leaching of large amounts of REE from red mud waste using strong acids over long digestion times seems feasible. However, after passing the "critical point" the sample usually becomes saturated and little or no alterations take place even if acid concentration, time or L/S ratio keeps increasing.

### **Future Suggestions:**

- Extensive datasets for REE and Ni and Cr are needed to further associate bauxites to their parent rocks.
- Isotope studies and dating of detrital minerals such as zircons and monazites would be help to further and more accurately identify the bauxite protoliths.
- Development of a model to assess pre bauxite formation processes and in situ REE enrichment parameters to predict REE concentrations. Such a model would be very helpful for REE exploration related to bauxite deposits. In addition it could help target selective mining and hence REE could be leached either directly from bauxite before the Bayer process or after it from red mud waste before it has been stockpiled.
- The application of a "CSM" protocol that is based on the well-accepted BCR technique will be able to extract the easily leachable REE phases in bauxite. This protocol should test Ce rich samples from the top of the bauxite profiles but also HREE enriched samples from the bottom of the profile in order to find out if the magnesium chloride or ammonium sulphate that extracts exchangeable cations works for both LREE and HREE.

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# **10. Appendices**

### Appendix A: Parnassus-Giona Zone Paleogeography and Tectonics

Parnassus-Giona zone from Middle Triassic up to Upper Cretaceous was an area in which took place a carbonate neritic sedimentation. More specifically, Middle-Upper Jurassic to Upper Cretaceous was the period during which took place the formation of the three bauxite horizons. The Parnassus-Giona zone at that time can be described as a shallow inland sea (lagoon), alternatingly influenced by both freshwater and seawater. These alterations were due to tectonic movements in addition to the change in climate of the area. Pindos sea was located in the western side of Parnassus, whereas in the eastern side, the Subpelagonian zone had already lifted up and ophiolites placed over it as nappes at the end of Jurassic (Celet and Clement, 1971; Combes, 1977, 1979).



Figure 10.1. Columnar sections of Parnassus-Giona and Subpelagonian zone (including the stratigraphic positions of the three bauxite horizons). I: Parnassus-Giona zone, II: intermediate section between Parnassus-Giona and Subpelagonian zone, and III: Subpelagonian zone (Greek Mining Enterprises Association, 1979).

A "crack" in the limits of Parnassus-Giona and Pelagonian zone was created during Upper Jurassic and after the formation of 2<sup>nd</sup> horizon bauxites. This graben was filled later on with the formation of the bauxites of the 3<sup>rd</sup> horizon and uplifted at the end of Lower Cretaceous. Hence, the continuity of these two zones was restored (Combes et al., 1981; Combes and Andreou, 1983) (Fig. 10.1).

Nowadays, the Parnassus-Giona zone is obducted over the Pindos formations. More precisely, the Upper Triassic limestones with *Megalodonta* and *Gyroporelles* are obducted onto the Pindos *Radiolarites* (near the Galaxeidi area). Moreover, the Triassic dolomites (in the Vardoussia area) are obducted onto the Pindos flysch. Similarly, many formations of the Pelagonian zone are obducted onto the Parnassus-Giona zone flysch (Agoriani, Souvala and Gerolakkos areas).

Many small and large-scale tectonic events acted between times at the area. The directions of major folds and faults that dominate the Parnassus-Giona zone are NNW-SSE and E-W. Tectonics also played a very important role in the formation of bauxites, as bauxites are placed uncomfortably on the limestone bedrocks, which are karstified. This fact indicates that before the formation of bauxite the area was lifted up and eroded for a long period time. More precisely, the right-stipping E-W striking faults are associated with the yellow and grey to whitish bauxites (Mariolakos et al. 1997, Laskou and Economou-Eliopoulos 2007).

The big orogenic movements that acted and are responsible for the lifting of the area are the Agassiz and the Neo-Cimmerian in Jurassic and the Sub-Hercynian and Laramide orogeny in Cretaceous. Furthermore, the Laramide orogeny is responsible for the uplifting and erosion of the area during the Albian, when the deposition of bauxitic material of the 3<sup>rd</sup> horizon took place.

In more detail, the Greek Orogen, which is part of the big Alpine Orogen, is proved to be a complex orogenic edifice created during different geological periods. Successive tectonic processes completed its final establishment during those periods.

Today is generally accepted that the Greek Orogen is consisting of the Cimmerian orogenic belt located at the internal part of the arc, the Alpine orogenic belt and the outer Mediterranean orogenic belt (Fig. 10.2). The first created before Upper Jurassic, the second during Cretaceous-Paleogene and the third one during Neogene (Miocene-Pliocene).

The alpine movements and deformations that shaped the Alpine orogeny are quite clear. Alpine Tectonics consists of two periods of tectonic events and processes, which are a period in Cretaceous and a period in Eocene-Oligocene. The geodynamic events and deforming episodes of the Alpine orogeny can be briefly summarized at the following figures (10.3 and 10.4).



Figure 10.2. Map showing the three orogenic belts of the Greek Orogen and their expansion in Asia (Mountrakis, 2010). The red point indicates the area of study.



Figure 10.3. Schematic sections representing the geodynamic evolution of Hellenides during the 1<sup>st</sup> period of the Alpine orogeny. It is also shown the oceanic-oceanic subduction of Neo-Tethys which leads to the formation of metamorphic sole, the subduction of oceanic crust beneath the Cimmerian-Eurasian continental crust, and the tectonic placement of ophiolites at the Cimmerian (Pelagonian) continental margin (Mountrakis, 2010). The red arrow shows approximately the area of study.



Figure 10.4. Schematic sections representing the geodynamic evolution of Helenides during the 2<sup>nd</sup> period of the Alpine orogeny. It is also shown the movements of tectonic plates, the subduction of Neo-Tethys ocean under the united continental plate, compressional tectonic stress (deformation-listric thrust faulting) and the thickening of the crust in the convergence position but also the tensile tectonic stress within the continent and the subsequent thinning of the crust, the uplifting of parts of the lower plate and finally the magmatic ascent (Mountrakis, 2010). The red arrow shows approximately the area of study.
### Appendix B: Bauxite Mining in Greece

Bauxite mining of is a key sector of the exploitation of Greek mineral wealth. For example, during 2011 the total bauxite production of the three bauxite mining companies operating in Greece was 2.3 Mt. S&B Industrial Minerals S.A. produced about 1 Mt per anum, followed by Delphi-Distomon S.A. (subsidiary of Aluminium S.A.), which produced approximately 750,000 t/year and exclusively feeds the parent company. Finally, Elmin S.A. produced the rest of bauxite but presents good prospective in increasing its production and exports in the future (Tsirambides and Filippidis, 2013). More recently, according to the BGS (Brown et al. 2014), Greece slightly decreased the bauxite production for 2012 and produced 1.8 Mt., whereas for 2013 produced 2.0 Mt according to the USGS (Lee-Bray, 2014) respectively.

The most well known bauxite deposits are located in an area that is delimited in the Helicon, Parnassus, Giona and Iti mountains. Bauxite reserves are approximately estimated about 100 million tons (O'Driscoll, 2011), whereas the indicative aluminum stocks in Greece are estimated about 2.5 Mt and their gross value is approximately about 3 billion pounds (£). Aluminium S.A. is the largest bauxite consumer bauxite in Greece producing more than 1.5 Mt/year. Bauxite used comes from Delphi-Distomon S.A., S&B S.A. and imports from Turkey. Moreover, Aluminium S.A. uses approximately 0.3 Mt of tropical bauxite for Bayer process, which is usually imported from Africa, Brazil, ect. Today, Aluminium S.A. annual production is about 810,000 t alumina, from which 490,000 t are exported and 320,000 are used for the aluminium production. These produce approximately165,000 tons of aluminum, from which 100,000 t are again exported, while the remaining 65,000 t are sold in the Greek market.

Nowadays, only 10% of total bauxite extraction is carried out by surface bauxite mining in Greece, and the remaining 90% involves underground mining. The vast majority of surface bauxite occurrences have already been mined in the past, therefore there are left only a few small surface bauxite deposits, operating now or are going to be exploited in the future.

Surface bauxite deposit exploitation operations are taking place by extracting the bauxite at grades in an open pit (Fig. 10.5). As in any type of surface ore extraction, the exposure of the deposit comes first and subsequently follows the extraction of the ore. More specifically, the "upright grades" method is used for uncovering the deposits in opencast mines, where

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step or vertical mining fronts are formed until ore is reached. Ore and sterile material extraction from the bauxite deposits is taking place by using explosives where is required. When bauxite is very soft and crumbly the mining is done directly by using wheel tractor-scrapers, dozers or loaders (Fig. 10.6).



Figure 10.5. Upright karst forms beneath a steeply dipping bauxite deposit. Anthimos open pit (Distomon, Central Greece) (Bárdossy, 1982). 1) Tithonian limestone, 2) bauxite and 3) Upper Jurassic limestone.



Figure 10.6. Delphi-Distomon S.A. wheel loader conveying bauxite ore (left) and underground loader in front of a bauxite pillar, during sampling at an underground Delphi-Distomon mine (right).

However, regarding the B3 (upper horizon bauxite) deposits (where bauxite is usually very hard) mining requires blasting. In such cases, there are

used crushing-rotary or hydraulic drill trucks to drill blast-holes. The most common explosives used for blasting are ANFO, gelatin dynamite and ammonite (Fig. 10.7 and 10.8). After blasting the material is loaded and conveyed for further processing.



Figure 10.7. Use of explosives at Delphi-Distomon S.A mines.



Figure 10.8. Use of dynamite and ANFO at Delphi-Distomon S.A. bauxite.

As far as the underground bauxite mining is concerned, two are the most common methods used in bauxite deposits of Greece. "Room-and-pillar" mining method is primarily used, but the "sublevel-caving" method is used in some cases as well. Two main types of deposits occur, in the form of lenses and in the form of dolines. There are also some smaller deposits in the form of pockets. An elongation of deposits mainly in NE-SW direction can be observed (Petraschek and Mack, 1978). The shape of dolines is elliptic or circular while their diameter ranges from 50 to about 250 meters, but in some cases can reach up to 1000 m. The walls of dolines are usually very steep (Fig. 10.9). The deepest dolines tend to lie at the crossing of faults. Many deposits are formed along fault lines. Therefore, tectonic fracturing of the bedrock is also an

essential factor in bauxite accumulation.

Lens-shaped deposits have various sizes. Their length ranges from 100 to 500 m., while their width is about 100-200m. The thicknesses of deposits are also diverse. There are occurrences of lenticular deposits with thickness from 2.4 m up to 30-35 m. Deposits with larger thicknesses usually have sharp wedges. Footwall surface of the deposits is irregular because of the limestone karst. The karst cavities in many cases reach 35 m. in depth. More intense karstification is observed along fault surfaces.



Figure 10.9. Composite sinkhole-type deposit cluster at Parnassus-Giona (Nia, 1968; Bárdossy, 1982). 1) Turonian-Senonian limestone, 2) bauxite and 3) Cenomanian limestone.

"Room and pillar" method belongs to the open stopes exploitation methods and is characterized by the fact that the empty spaces created during the excavation remain open due to the physical support provided by the rocks. This method is applied at horizontal to moderate slope layered deposits of a sufficient strength, it is not depend on the deposit's thickness, but needs to be located in small to medium depth and have a durable hanging wall.

More precisely, the slope of the layers should be below  $30^{\circ}$  while the thickness usually reaches about 10 m. If the bauxite deposit thickness is greater than 10 m, then the "room and pillar" method is used with the dry sterile ore gangue material (tailings) to be used as backfill (Fig. 10.10).

The access to the deposit is made by at least two declines/adits needed for both conveying the mined ore and for the necessary ventilation (Fig. 10.11). In most bauxite deposits of Greece the accessing usually takes place by two declines. The first is located at the lowest level of the deposit and is used for removing the ore to the surface (footwall decline). The second one is positioned at a higher level and is normally used for setting the ventilation facilities of the mine.



Figure 10.10. The "Room and pillar" extraction method in horizontal (A), inclined (B) and very thick mine (C) (De Souza, 2010).



Figure 10.11. Decline portal (left) and air and smoke circulating in the galleries of a Delphi-Distomon underground mine after a blast (right).

It is worth mentioning that the shape and the position of the pillars are usually not uniform. That is because mining engineers tend to seek the poorest in ore positions of the deposit to place them. Pillars remaining in a deposit are by default a loss in useful material. For this reason, it is often used to reduce the pillar size during the final phase of the exploitation (retreat) in order to maximize the extraction rate (Fig. 10.12).



Figure 10.12. Typical bauxite pillars at Delphi-Distomon S.A. underground mines.

Finally, for bauxite deposits whose gradient exceeds 60°, the method of "sublevel-caving" is applied for extraction, but concerns only a very small number of deposits in Greece. During this process the extraction is carried out in successive levels. The lower part is detached by using explosives, while the upper part precipitates. The advantages of this method are mainly the low cost and mineralization of necessary preparatory works required. Despite the extraction percentage of this method that is of the order of 70-75%, the major problem is the blending of bauxite (the ore is contaminated by the precipitating sterile calcareous material).

The access is made by horizontal or inclined tunnels depending on the morphology of the location of the deposit. From access tunnels there are excavated trapezoidal-shape production galleries of 14 m<sup>2</sup> acreage (4 m wide and about 3-3,5 m high) to the direction of the deposit and usually in contact with limestone hanging wall. These galleries might be supported by timber where it is required. Hence, there are gradually created levels, which are spaced apart approximately 10 to 12 m. Extraction in each level starts from the edges and retreats towards the central access point.





Figure 10.13. XRD patterns and interpretations for sample M1 S3 and its duplicate.



Figure 10.14. XRD patterns and interpretations for sample M1 S6 and its duplicate.





Figure 10.15. XRD patterns and interpretations for sample M2 S3 and its duplicate.



Figure 10.16. XRD patterns and interpretations for sample M2 S8 and its duplicate.



Figure 10.17. XRD patterns and interpretations for sample M3 S4 and its duplicate.



Figure 10.18. XRD patterns and interpretations for sample M3 S9 and its duplicate.



Figure 10.19. XRD patterns and interpretations for sample M4 S1 and its duplicate.



Figure 10.20. XRD patterns and interpretations for sample M4 S10 and its duplicate.

### Appendix D: Whole Rock Analysis Supplementary

Wt.%	Jan	Feb	Mar	Apr	Мау	Jun	Jul	Aug	Sep	Oct	Νον	Dec	Avg
Al <sub>2</sub> O <sub>3</sub>	58.35	58.93	59.42	58.96	58.57	59.07	58.22	58.74	58.36	58.59	58.11	58.27	58.64
Fe <sub>2</sub> O <sub>3</sub>	21.00	21.09	20.79	20.86	21.32	21.43	21.62	21.08	21.14	21.04	21.39	21.68	21.20
SiO <sub>2</sub>	2.88	2.44	2.35	2.46	2.41	2.35	2.69	3.27	2.83	3.25	3.25	2.07	2.77
TiO <sub>2</sub>	2.77	2.66	2.83	2.77	2.66	2.69	2.64	2.62	2.69	2.72	2.74	2.73	2.58
CaO	1.52	1.44	1.53	1.75	1.83	1.48	1.48	1.29	1.71	1.39	1.50	1.26	1.52
S	0.10	0.05	0.05	0.05	0.04	0.04	0.04	0.10	0.04	0.04	0.04	0.04	0.05
LOI	12.77	12.94	12.61	12.67	12.54	10.54	12.41	12.28	12.56	12.36	12.30	12.09	12.34
Total	99.39	99.55	99.58	99.52	99.37	96.60	99.10	99.38	99.33	99.39	99.33	98.14	
Production (tones)	47749.38	43520.64	50725.42	42378.78	53653.52	47229.24	49810.79	47545.32	44641.86	52995.34	45447.64	44284.82	47498.56

Table 10.1a. Quantified major element analysis of the bauxite ore mined during 2012 by Delphi-Distomon S.A.

Note: The total bauxite ore mined for the year 2012 was 569,982.75 tones.

Table 10.1b. Quantified major element analysis of the bauxite ore mined during 2011 by Delphi-Distomon S.A.

Wt.%	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Avg
Al <sub>2</sub> O <sub>3</sub>	60.34	59.69	59.31	59.32	59.45	58.66	59.29	59.19	58.57	58.69	58.74	58.65	59.16
Fe <sub>2</sub> O <sub>3</sub>	20.60	20.49	20.69	20.70	20.27	20.90	20.58	21.28	21.34	21.30	21.21	21.37	20.90
SiO <sub>2</sub>	2.39	2.66	2.69	2.69	2.55	2.72	2.66	2.73	2.73	2.54	2.67	2.93	2.66
TiO <sub>2</sub>	2.79	2.72	2.75	2.68	2.76	2.67	2.76	2.70	2.67	2.70	2.74	2.77	2.59
CaO	1.14	1.54	1.63	1.35	1.34	1.56	1.39	1.11	1.46	1.64	1.43	1.42	1.42
S	0.07	0.08	0.09	0.09	0.08	0.09	0.07	0.10	0.06	0.05	0.11	0.10	0.08
LOI	12.34	12.44	12.38	12.47	12.61	12.58	12.71	12.16	12.63	12.69	12.39	12.10	12.46
Total	99.67	99.62	99.54	99.30	99.06	96.18	99.46	99.27	99.46	99.61	99.29	98.34	
Production (tones)	45765.98	40921.16	53235.80	47501.74	45653.24	40542.82	46638.56	47530.16	52638.76	47247.00	41817.40	43975.66	46122.36

Note: The total bauxite ore mined for the year 2011 was 553,468.28 tones.

Table 10.2. Semi-quantitative chemical composition of bauxite ores determined by XRF.

Wt.%	M1	M1	M2	M2	M3 S4	M3 S9	M4	M4	Min	Max	Avq	Std
	<b>S</b> 4	56	51	57	Dupi	Dupi	54	59			Ŭ	Dev
$AI_2O_3$	55.66	54.20	51.31	48.58	60.85	52.93	56.43	58.53	48.58	60.85	54.81	3.94
Fe <sub>2</sub> O <sub>3</sub>	16.67	16.06	18.70	21.07	17.46	19.61	16.59	14.88	14.88	21.07	17.63	2.03
TiO <sub>2</sub>	3.43	3.30	3.83	3.30	3.39	2.72	3.32	3.62	2.72	3.83	3.36	0.32
SiO <sub>2</sub>	0.63	2.04	2.03	2.09	2.81	10.20	0.92	1.12	0.63	10.20	2.73	3.10
CaO	0.03	0.10	0.13	0.09	0.07	0.13	0.07	0.07	0.03	0.13	0.09	0.03
SO <sub>3</sub>	0.33	0.24	0.63	0.23	0.33	1.48	0.25	0.22	0.22	1.48	0.46	0.43
MnO	0.00	0.00	0.03	0.00	0.02	0.00	0.00	0.01	0.00	0.03	0.01	0.01
MgO	0.00	0.08	0.00	0.00	0.09	0.19	0.00	0.00	0.00	0.19	0.05	0.07
Na₂O	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.12	0.02	0.04
P <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.03	0.00	0.00	0.02	0.01	0.02	0.00	0.03	0.01	0.01
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.08	0.44	0.00	0.00	0.00	0.44	0.07	0.15
LOI	12.34	12.82	14.09	11.78	11.94	11.75	12.30	12.84	11.75	14.09	12.48	0.77
Total	89.40	89.17	91.31	87.58	97.59	100.09	90.25	91.71	78.81	112.46	91.72	4.38
Ррт												
Cr <sub>2</sub> O <sub>3</sub>	1650	1720	1490	1220	1220	1050	1650	1430	1050	1720	1429	244
NiO	257	370	1050	836	1920	1650	232	192	192	1920	813	677
V <sub>2</sub> O <sub>5</sub>	630	570	1530	900	1610	1620	970	1070	570	1620	1113	427
ZrO <sub>2</sub>	560	563	590	536	537	439	548	590	439	590	545	48
NbO <sub>5</sub>	54	54	70	58	50	50	55	59	5	70	56	6
ZnO	0	0	0	0	145	180	0	0	0	180	41	76
$Ga_2O_3$	0	0	70	0	70	0	80	70	0	80	36	39
$As_2O_3$	0	0	447	130	0	0	0	0	0	447	72	158
SrO	0	0	40	0	30	54	30	30	0	54	23	21
CeO <sub>2</sub>	0	0	0	650	0	0	0	530	0	650	148	275

Note: The results are not normalized to 100%. Values in grey italics were quantified with exactly the same method used for the rest of the elements, but not definitively identified as present by the software. This is due to the small peak height and shape that is debatable on whether or not the indication can be 100% interpreted as element's presence. Zero valued elements or other missing trace elements are below XRF detection limits, which are from % to ppm but are also element, sample and mode dependent.



## SARM - Service d'Analyses des Roches et des Minéraux





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#### Reference Material BX-N Bauxite

Major Elements	5				Trace Eleme	nts			
%	WV	sd	±CLs	Ν	µg.g⁻¹	wv	sd	±CLs	
SiO <sub>2</sub>	7.40	0.46	0.15	37	Hf	15.2	4	1.1	
Al <sub>2</sub> O <sub>3</sub>	54.21	1.16	0.4	34	Но	4.1	-	0.5	
Fe <sub>2</sub> O <sub>3</sub>	22.88	1	0.6	11				0.0	
FeO	0.26	0.21	0.13	11	In	0.3		DV	
MnO	0.05	0.02	0.009	20		0.0	-	þv	
MaO	0 11	0.08	0.03	29	1.2	255	76	10	
CaO	0 17	0 14	0.05	34		20	10 71	0	
Na.O	0.04	0.06	0.00	24		10	12.71	9	
K.O	0.05	0.00	0.02	24	Lu	1.0	0.44	0.18	
	0.05	0.03	0.01	20			0.50		
R O	2.31	0.23	0.09	29	WO	8.3	2.56	0.7	
205	0.13	0.06	0.03	18					
H <sub>2</sub> O	11.48	0.22	0.15	9	Nb	52	5.28	4	
H <sub>2</sub> O <sup>-</sup>	0.44	0.09	0.07	7	Nd	163	30.51	7	
CO2	0.44	0.23	0.19	6	Ni	180	36.77	16	
Fe <sub>2</sub> O <sub>3</sub> T	23.17	0.84	0.28	36					
LOI	12.17	0.26	pv	18	Pb	135	76.49	13	
					Pr	54	-	3.5	
Trace Elements	5		<i></i>						
ug.g <sup>-1</sup>	wv	sd	±CLs	N	RD	3.6	11.04	0.6	
					Sb	8	23.32	pv	
As	115	8.96	6	10	Sc	60	10.32	7	
					Sm	22	3.4	1.3	
Ва	30	26.38	9	11	Sn	13.4	10.98	1.1	
Be	5.5	0.87	0.6	7	Sr	110	18.68	9	
Bi	1.7	-	pv	-				-	
_					Та	4.6	0.84	0.4	
Ce	520	43	23	13	Tb	3	0.33	0.3	
Co	30	33.12	7	21	Th	50	10.76	6	
Cr	280	74.9	31	22	Tm	1.7	-	0.2	
Cs	0.4	-	pv	-					
Cu	18	4.22	2	17	U	8.8	2.42	1.5	
Dу	18.5	-	1.4	1	v	350	77.06	44	
Ēr	11	-	1	-	w	9		1	
Eu	4.4	0.53	0.3	10	10.0	-			
					Y	114	40 24	14	
-	900	100	pv	6	Yb	11.6	2.12	1.5	
la	67	18 99	14	7	Zn	80	20 04	15	
Gd	20	6.35	1.6	5	7.	550	30.04 90 EF	10	
Ge	11	0.00	0.0	0	<b>~</b> 1	330	00.00	44	
		-	P4						

Modified from : Govindaraju K. (1994) Geostandards Newsletter, Vol XIX Special Issue, July 1995

List of abbreviations

N - Number of results	sd - Standard deviation	WV - Working value	
CLs - 95% Confidence limits	LOI - Loss on ignition	pv - Proposed value	

CRPG-CNRS : 15, rue Notre-Dame-des-Pauvres, BP 20. 54501 Vandoeuvre-les-Nancy. France Tél : 33 (0)3 83 59 42 00. Fax : 33 (0)3 83 51 17 98 - http://www.crpg.cnrs-nancy.fr



Sample Name	Ag	As	Ва	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
BX-N 1	0.1	121.4	20.6	7.5	1.5	0.0	23.3	262.6	19.3	64.8	6.2	12.6	10.0	59.5	163.0	102.9	0.7	9.7	55.1	9.5	36.2	7.4	332.9	134.3	60.0	492.6
BX-N 2	0.1	121.9	19.8	8.2	1.4	0.0	22.8	259.5	17.0	64.1	6.3	12.6	9.6	58.6	160.5	101.8	0.6	9.3	61.4	8.8	32.6	7.1	321.2	132.4	60.4	489.2
BX-N 3	0.2	120.6	17.1	7.3	2.0	0.0	21.3	262.4	16.1	61.0	7.0	14.4	11.2	91.5	152.0	90.4	0.4	18.9	54.9	34.8	38.3	7.1	344.0	30.6	43.3	393.6
BX-N 4	0.1	129.8	12.6	6.8	1.5	0.0	23.5	285.2	16.3	62.4	5.7	10.4	10.4	70.6	162.2	96.0	0.0	12.5	50.8	16.2	33.2	7.1	360.4	20.1	48.3	390.0
BX-N 5	0.2	125.1	13.2	9.6	1.5	0.0	21.6	282.6	17.0	59.6	5.1	9.8	9.9	67.1	156.5	90.9	0.0	10.0	44.7	10.1	27.7	6.8	359.7	15.6	49.3	389.8
BX-N 6	0.2	129.7	14.2	9.2	1.5	0.0	23.6	299.3	16.5	65.0	5.5	10.2	10.2	68.0	167.2	94.3	0.0	10.1	49.2	9.6	30.5	7.2	383.5	13.3	51.3	403.8
Average	0.2	124.8	16.3	8.1	1.6	0.0	22.7	275.3	17.0	62.8	6.0	11.7	10.2	69.2	160.2	96.1	0.3	11.7	52.7	14.8	33.1	7.1	350.3	57.7	52.1	426.5
Reference Value	N/A	115.0	30.0	5.5	1.7	N/A	30.0	280.0	18.0	67.0	1.1	15.2	8.3	52.0	180.0	135.0	3.6	8.0	110.0	4.6	50.0	8.8	350.0	9.0	80.0	550.0
(Avg-Std)/Std %	N/A	8.5	- 45.8	47.4	- 6.1	N/A	- 24.4	-1.7	-5.4	-6.2	441.7	- 23.2	23.0	33.1	-11.0	-28.8	- 92.1	46.6	-52.1	222.5	- 33.8	- 19.0	0.1	541.3	- 34.8	-22.5

Table 10.3a. Trace element recovery values (ppm) of BX-N samples dissolved by the CSM 4 acid attack method.

Table 10.3b. REE recovery values (ppm) of BX-N samples dissolved by the CSM 4 acid attack method.

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
BX-N 1	42.2	58.2	185.4	12.5	40.3	6.9	1.4	5.9	0.9	6.6	1.3	4.3	0.7	4.6	0.7	32.5
BX-N 2	43.1	63.7	170.9	13.4	43.2	7.3	1.5	6.1	0.9	6.3	1.3	4.1	0.6	4.5	0.7	30.2
BX-N 3	41.3	71.5	156.7	14.5	45.1	6.5	1.3	5.3	0.8	5.4	1.1	3.3	0.6	3.5	0.6	24.3
BX-N 4	42.4	33.2	113.7	7.6	25.5	4.4	0.9	3.8	0.5	4.3	0.9	2.8	0.4	3.0	0.5	18.1
BX-N 5	34.4	29.3	102.1	6.9	22.7	4.1	0.9	3.5	0.6	3.9	0.9	2.6	0.5	2.8	0.5	17.0
BX-N 6	35.4	34.8	120.1	7.6	25.1	4.4	1.0	3.8	0.6	4.2	0.9	2.8	0.5	2.9	0.5	18.5
Average	39.8	48.5	141.5	10.4	33.6	5.6	1.2	4.7	0.7	5.1	1.1	3.3	0.5	3.5	0.6	23.4
Reference Value	60.0	355.0	520.0	54.0	163.0	22.0	4.4	20.0	3.0	18.5	4.1	11.0	1.7	11.6	1.8	114.0
(Avg-Std)/Std %	-33.7	-86.3	-72.8	-80.7	-79.4	-74.5	-73.8	-76.3	-75.9	-72.4	-73.9	-69.8	-67.9	-69.4	-67.4	-79.5



Figure 10.22. BSE pictures of bauxite residue from various samples (left) and their EDS spectra (right).



Figure 10.23. BSE picture of calcinated grain in red mud waste residue (left) and its EDS spectrum (right).



Figure 10.24. BSE pictures of red mud waste residue from various samples (left) and their EDS spectra (right).



Figure 10.25. BSE picture of undissolved magnesiochromite crystal in red mud waste residue (left) and its EDS spectrum (right).



Figure 10.26. BSE pictures of undissolved detrital zircon crystals in bauxite (upper left) and red mud waste (lower left) residue and their EDS spectra (right).

Table 10.4a. Trace element recovery values (ppm) of BX-N samples prepared using the NHM method – dissolution procedure (increased HF

and digestion time).

Sample Name	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
BX-N 1	0.4	110.2	31.9	6.5	5.8	0.2	37.4	300.1	19.0	93.8	16.7	20.6	36.7	91.2	201.7	150.2	2.4	30.9	91.4	29.0	73.4	9.5	399.8	58.2	101.5	388.4
BX-N 2	0.2	110.3	30.4	5.4	5.5	0.2	39.0	307.5	17.7	96.6	17.6	12.5	24.8	74.2	205.4	162.0	2.2	19.0	94.1	19.6	53.6	9.3	412.5	38.4	100.5	396.0
BX-N 3	0.2	102.6	31.5	5.5	2.8	N/A	36.8	293.5	16.1	96.1	16.5	10.9	18.8	66.3	197.2	145.4	1.8	14.2	98.2	16.0	49.6	8.8	393.9	27.5	81.4	374.1
BX-N 4	0.2	110.4	31.2	5.6	2.5	0.2	38.4	307.3	16.9	98.7	19.0	11.0	16.6	67.0	204.9	150.7	1.8	12.9	100.9	14.6	50.5	9.3	409.6	22.7	87.7	394.0
BX-N 5	0.1	107.9	31.6	5.0	2.4	0.1	38.1	303.5	15.9	100.1	17.8	10.3	14.4	64.8	206.7	148.6	2.0	12.0	95.4	12.4	49.3	9.1	408.2	18.4	86.1	383.8
BX-N 6	0.1	109.0	32.0	6.1	2.3	0.2	38.9	311.1	16.1	100.8	18.1	10.6	13.6	65.2	207.9	154.4	1.6	11.8	99.0	11.7	49.0	9.2	415.0	17.0	91.4	391.8
BX-N 7	0.1	104.3	30.8	5.6	2.3	0.7	38.6	309.6	17.1	98.0	17.7	10.2	12.6	63.8	206.8	151.8	1.2	10.8	95.8	10.6	48.4	9.2	415.1	14.0	85.9	387.9
BX-N 8	0.1	111.5	31.4	5.8	2.1	0.0	38.7	309.3	17.4	104.7	20.5	10.1	12.0	64.9	203.0	148.6	1.7	10.6	114.8	11.4	50.6	9.1	406.8	13.1	91.1	389.6
BX-N 9	0.1	104.7	30.1	5.8	2.0	0.3	39.2	297.7	18.6	101.0	18.6	10.5	11.4	62.4	205.8	150.5	1.9	9.8	99.0	9.2	47.8	9.0	409.7	12.1	96.5	401.2
BX-N 10	0.0	107.8	30.9	5.4	2.0	0.2	37.9	294.5	14.0	100.5	18.9	10.2	11.2	61.9	202.7	146.6	1.4	9.4	100.5	8.9	47.3	9.0	405.3	11.5	75.4	394.6
Average	0.1	107.9	31.2	5.7	3.0	0.2	38.3	303.4	16.9	99.0	18.1	11.7	17.2	68.2	204.2	150.9	1.8	14.1	98.9	14.3	52.0	9.1	407.6	23.3	89.7	390.1
Reference Value	N/A	115.0	30.0	5.5	1.7	N/A	30.0	280.0	18.0	67.0	1.1	15.2	8.3	52.0	180.0	135.0	3.6	8.0	110.0	4.6	50.0	8.8	350.0	9.0	80.0	550.0
(Avg-Std)/Std %	N/A	-6.2	3.9	3.1	74.7	N/A	27.7	8.4	-6.3	47.8	1548.7	23.0	107.4	31.1	13.5	11.8	- 49.9	76.9	-10.1	211.5	3.9	3.8	16.5	158.9	12.2	-29.1

Table 10.4b. REE recovery values (ppm) of BX-N samples prepared using the NHM method – dissolution procedure (increased HF and digestion time).

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
BX-N 1	54.8	287.0	478.8	45.2	131.3	17.6	3.7	14.7	2.2	14.0	2.8	8.3	1.3	8.4	1.4	76.6
BX-N 2	51.3	298.1	494.4	46.8	135.7	17.9	3.4	15.4	2.3	14.1	2.9	8.7	1.3	8.8	1.4	78.3
BX-N 3	51.9	305.2	496.1	48.0	139.0	18.6	3.8	15.7	2.4	14.6	2.9	9.0	1.4	8.8	1.4	82.5
BX-N 4	55.6	312.8	514.5	48.7	141.0	19.3	3.8	16.0	2.4	15.3	2.9	9.1	1.4	9.3	1.4	83.1
BX-N 5	53.3	306.1	508.6	48.0	139.5	18.9	3.7	15.5	2.4	14.4	2.9	9.0	1.3	9.1	1.4	80.6
BX-N 6	51.8	301.3	497.8	47.7	138.9	18.7	3.7	15.3	2.4	14.2	2.9	8.9	1.3	8.9	1.4	80.4
BX-N 7	49.5	302.4	505.5	47.4	137.9	19.0	3.7	15.1	2.4	14.3	2.9	8.8	1.4	8.9	1.3	80.6
BX-N 8	64.1	363.2	567.1	55.7	158.4	21.5	4.3	17.7	2.8	16.6	3.3	10.2	1.5	10.2	1.5	97.0
BX-N 9	51.5	315.3	519.2	48.7	141.5	19.2	3.8	15.9	2.4	15.2	3.0	9.2	1.4	9.4	1.4	84.2
BX-N 10	52.5	315.7	515.6	48.8	141.8	18.5	3.8	15.5	2.4	14.6	3.0	9.3	1.4	9.2	1.4	85.3
Average	53.6	310.7	509.8	48.5	140.5	18.9	3.8	15.7	2.4	14.7	2.9	9.0	1.4	9.1	1.4	82.9
Reference Value	60.0	355.0	520.0	54.0	163.0	22.0	4.4	20.0	3.0	18.5	4.1	11.0	1.7	11.6	1.8	114.0
(Avg-Std)/Std %	-10.6	-12.5	-2.0	-10.2	-13.8	-14.0	-14.4	-21.6	-20.0	-20.3	-28.3	-17.8	-18.9	-21.6	-22.4	-27.3

Sample Name	Ag	As	Ba	Be	Bi	Cd	Со	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
BX-N 1	0.7	144.2	38.0	8.8	4.5	0.3	39.6	313.2	20.0	110.1	20.8	17.9	23.9	64.2	211.2	155.3	6.3	19.0	145.1	6.0	64.7	10.1	425.2	38.3	101.6	1121.4
BX-N 2	0.6	139.0	37.8	7.7	2.7	0.3	40.3	318.0	18.1	110.4	20.8	16.3	17.9	59.7	212.8	156.3	6.1	14.4	145.9	5.6	60.3	10.1	432.9	24.8	100.7	1225.0
BX-N 3	0.5	131.3	43.8	6.2	2.4	0.3	39.6	314.8	19.6	108.5	21.7	15.9	14.3	58.2	213.2	151.2	5.9	11.4	144.6	5.3	57.4	9.8	428.7	18.7	101.8	1003.2
BX-N 4	0.5	139.8	36.9	6.0	2.1	0.3	40.9	322.9	19.9	111.8	21.7	16.9	13.6	59.0	216.4	153.6	5.8	11.0	148.1	5.2	58.1	10.1	442.7	17.6	114.3	1513.3
BX-N 5	0.5	135.0	37.0	6.0	2.4	0.6	41.3	325.0	31.2	111.8	21.4	16.6	13.1	58.9	221.3	154.2	5.8	10.4	149.2	5.1	56.9	9.8	444.0	16.1	129.1	2081.3
BX-N 6	0.5	142.8	37.3	5.4	2.0	0.4	41.4	334.5	18.1	114.8	23.0	17.7	12.3	61.3	219.1	153.6	5.6	10.4	148.7	5.1	58.0	10.0	451.8	15.9	131.1	1411.6
BX-N 7	0.5	137.3	37.4	6.4	2.0	0.3	40.8	327.2	19.6	112.9	20.9	16.4	11.5	58.9	215.6	150.6	6.2	9.6	152.4	5.0	56.5	9.8	444.9	12.9	117.1	1678.6
BX-N 8	0.6	139.3	35.3	6.5	1.9	0.2	40.9	325.3	17.6	111.6	21.7	17.1	10.9	59.7	216.5	149.2	5.7	9.5	147.2	4.9	56.2	9.6	440.5	10.4	97.4	1450.5
BX-N 9	0.4	135.5	40.1	7.0	1.8	0.2	40.9	324.3	18.0	109.2	22.0	15.4	10.6	58.9	218.9	148.5	6.0	9.4	147.5	4.8	53.9	9.4	437.8	12.5	440.7	1515.1
BX-N 10	0.6	138.6	37.3	8.1	1.9	0.3	41.2	334.4	16.6	113.1	22.4	17.0	10.8	61.1	226.5	153.4	6.5	9.7	149.9	4.9	56.6	9.7	453.6	11.0	314.0	1661.7
Average	0.5	138.3	38.1	6.8	2.4	0.3	40.7	324.0	19.9	111.4	21.7	16.7	13.9	60.0	217.2	152.6	6.0	11.5	147.9	5.2	57.9	9.8	440.2	17.8	164.8	1466.2
Reference Value	N/A	115.0	30.0	5.5	1.7	N/A	30.0	280.0	18.0	67.0	1.1	15.2	8.3	52.0	180.0	135.0	3.6	8.0	110.0	4.6	50.0	8.8	350.0	9.0	80.0	550.0
(Avg-Std)/Std %	N/A	20.3	27.0	23.6	39.7	N/A	35.6	15.7	10.4	66.3	1869.0	10.1	67.4	15.4	20.6	13.0	66.2	43.5	34.4	13.0	15.7	11.7	25.8	98.0	106.0	166.6

Table 10.5a. Trace element recovery values (ppm) of BX-N samples prepared using the Na<sub>2</sub>O<sub>2</sub> sintering – dissolution procedure.

Table 10.5b. REE recovery values (ppm) of BX-N samples prepared using the  $Na_2O_2$  sintering – dissolution procedure.

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
BX-N 1	82.9	417.8	624.6	62.5	186.6	25.0	4.9	22.1	3.6	21.9	4.4	13.5	2.0	13.4	2.1	133.1
BX-N 2	82.9	421.2	638.3	62.7	187.5	25.7	5.1	22.0	3.7	21.8	4.4	13.5	2.0	13.4	2.1	134.0
BX-N 3	78.9	416.7	624.6	62.1	184.3	24.6	5.0	21.3	3.5	21.1	4.4	13.3	1.9	13.4	2.0	132.7
BX-N 4	85.4	422.0	637.9	63.2	184.3	24.8	5.1	21.7	3.6	22.1	4.5	13.4	2.0	13.6	2.0	138.1
BX-N 5	92.6	424.6	632.7	63.1	186.2	25.1	4.9	22.0	3.6	22.0	4.5	13.4	2.0	13.3	2.0	137.1
BX-N 6	88.5	430.8	659.1	63.8	188.7	25.6	5.1	22.1	3.6	22.2	4.5	13.6	2.0	13.7	2.0	139.0
BX-N 7	88.6	422.5	634.3	63.1	185.5	24.8	5.0	21.5	3.6	21.8	4.4	13.3	2.0	13.3	2.0	136.4
BX-N 8	85.1	422.3	629.0	62.5	184.9	24.7	4.9	21.5	3.5	21.8	4.4	13.3	2.0	13.4	2.0	136.1
BX-N 9	83.5	415.2	614.0	61.8	182.1	23.7	4.7	21.1	3.5	21.2	4.3	12.9	1.9	12.9	1.9	133.3
BX-N 10	92.5	429.5	656.9	63.2	187.9	26.0	4.9	22.2	3.6	21.6	4.4	13.5	2.0	13.6	2.0	139.9
Average	86.1	422.3	635.2	62.8	185.8	25.0	5.0	21.8	3.6	21.8	4.4	13.4	2.0	13.4	2.0	136.0
Reference Value	60.0	355.0	520.0	54.0	163.0	22.0	4.4	20.0	3.0	18.5	4.1	11.0	1.7	11.6	1.8	114.0
(Avg-Std)/Std %	43.5	18.9	22.1	16.3	14.0	13.6	12.9	8.8	19.4	17.6	7.4	21.6	16.1	15.5	11.2	19.3

Sample Name	Ba	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	V	W	Zr
BX-N 1	29.0	9.0	33.1	0.6	57.7	14.5	52.2	3.5	14.0	118.3	3.9	51.2	9.1	380.0	7.2	521.5
BX-N 2	29.0	8.0	33.7	0.4	55.3	14.7	50.3	3.4	13.0	112.7	3.9	50.1	8.9	367.0	8.0	505.1
Average	29.0	8.5	33.4	0.5	56.5	14.6	51.3	3.5	13.5	115.5	3.9	50.7	9.0	373.5	7.6	513.3
Reference Value	30.0	5.5	30.0	0.4	67.0	15.2	52.0	3.6	13.4	110.0	4.6	50.0	8.8	350.0	9.0	550.0
(Avg-Std)/Std %	-3.3	54.5	11.3	25.0	-15.7	-3.9	-1.4	-4.2	0.7	5.0	-15.2	1.3	2.3	6.7	-15.6	-6.7

Table 10.6a. Trace element recovery values (ppm) of BX-N samples prepared using the lithium borate fusion – dissolution procedure.

Table 10.6b. REE recovery values (ppm) of BX-N samples prepared using the lithium borate fusion – dissolution procedure.

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Υ
BX-N 1	371.5	585.1	55.9	162.2	21.3	4.2	20.1	3.0	18.6	3.7	10.7	1.7	11.3	1.7	114.0
BX-N 2	357.1	551.9	53.0	155.3	20.6	4.2	18.6	3.0	17.5	3.7	10.0	1.6	10.6	1.6	109.6
Average	364.3	568.5	54.4	158.8	20.9	4.2	19.3	3.0	18.0	3.7	10.4	1.6	10.9	1.7	111.8
<b>Reference Value</b>	355.0	520.0	54.0	163.0	22.0	4.4	20.0	3.0	18.5	4.1	11.0	1.7	11.6	1.8	114.0
(Avg-Std)/Std %	2.6	9.3	0.8	-2.6	-4.9	-4.3	-3.5	-1.0	-2.6	-10.4	-5.8	-3.2	-5.6	-7.2	-1.9

Note: The element recovery percentages seem to confirm the total dissolution of samples by Li B fusions. The majority of the (Average-Standard/Standard)% values are very close to zero. However, some higher values are due to the extremely small concentrations of some elements, meaning that very small differences can produce very high % variations. Moreover, some of the high (Average-Standard/Standard)% values are because of the high standard deviation and confidence limits that some of the certified reference material elements have (Fig. 10.21).

Sample Name	Ва	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	V	W	Zr
STD SO-18 1	492	<1	25.4	6.3	16.2	9.3	19.2	27.5	14	404.7	6.4	9.4	16.2	209	15.2	296.1
STD SO-18 2	496	<1	23.4	6.9	16.1	9.6	18.5	27.6	14	399.1	7	9.5	16.7	200	14.3	295.1
STD SO-18 3	515	<1	26.4	6.6	16.1	9.9	20	28.3	14	420	6.9	9.3	15.5	212	14.8	300.8
STD SO-18 4	532	2	26.6	7	15.3	9.3	19.4	27.7	15	415.4	6.6	10.2	15.9	210	14.8	305.1
STD SO-18 5	514	<1	25.8	6.6	15.8	9.4	19.9	26.9	14	411.6	6.9	8.7	16.2	200	14.5	301.2
STD SO-18 6	536	<1	27.6	6.4	16.7	9.7	19.7	27.3	15	415.1	6.4	9.4	15.4	220	15.1	293.9
Average	514.2	<1	25.9	6.6	16.0	9.5	19.5	27.6	14.3	411.0	6.7	9.4	16.0	208.5	14.8	298.7
<b>Reference Value</b>	514.0	1.0	26.2	7.1	17.6	9.8	19.3	28.7	15.0	407.4	7.4	9.9	16.4	200.0	14.8	290.0
(Avg-Std)/Std %	0.0	<1	-1.3	-6.6	-8.9	-2.7	0.8	-4.0	-4.4	0.9	-9.5	-4.9	-2.5	4.3	-0.1	3.0

Table 10.7a. Trace element recovery values (ppm) of STD SO-18 samples prepared using the lithium borate fusion – dissolution procedure.

Table 10.7b. REE recovery values (ppm) of STD SO-18 samples prepared using the lithium borate fusion – dissolution procedure.

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
STD SO-18 1	12.9	26.7	3.2	13.2	2.7	0.9	2.9	0.5	3.0	0.6	1.7	0.3	1.7	0.3	28.4
STD SO-18 2	13.5	26.6	3.1	12.6	2.7	0.8	2.7	0.5	2.8	0.6	1.7	0.3	1.6	0.3	29.2
STD SO-18 3	12.9	27.7	3.3	12.6	2.6	0.9	2.9	0.5	3.0	0.6	1.9	0.3	1.7	0.3	30.2
STD SO-18 4	12.5	26.6	3.2	12.6	2.8	0.8	2.9	0.5	2.9	0.6	1.7	0.3	1.7	0.3	30.8
STD SO-18 5	12.7	27.9	3.2	12.8	2.9	0.8	2.9	0.5	3.0	0.6	1.8	0.3	1.8	0.3	30.5
STD SO-18 6	13.3	28.1	3.3	13.0	2.8	0.8	3.0	0.5	2.8	0.6	1.7	0.3	1.7	0.3	28.2
Average	13.0	27.3	3.2	12.8	2.7	0.9	2.9	0.5	2.9	0.6	1.7	0.3	1.7	0.3	29.6
Reference Value	12.3	27.1	3.5	14.0	3.0	0.9	2.9	0.5	3.0	0.6	1.8	0.3	1.8	0.3	29.0
(Avg-Std)/Std %	5.4	0.6	-6.7	-8.6	-8.9	-3.6	-1.9	-10.1	-2.9	-5.6	-5.2	-3.7	-4.9	-4.3	1.9

Note: The element recovery percentages seem to confirm the total dissolution of samples by Li B fusions. The majority of the (Average-Standard/Standard)% values are very close to zero. However, some higher values are due to the extremely small concentrations of some elements, meaning that very small differences can produce very high % variations.

# Table 10.8a. Trace element recovery values (ppm) of bauxite samples prepared using the lithium borate fusion – dissolution procedure in comparison with the 4 acids attack.

Sample	Ba	Ba	Dissolv	Be	Be	Dissolv	Co	Co	Dissolv	Ga	Ga	Dissolv	Hf	Hf	Dissolv	Nb	Nb	Dissolve	Rb	Rb	Dissolv
Name	(ACME)	(CSM)	ed %	(ACME)	(CSM)	ed %	(ACME)	(CSM)	ed %	(ACME)	(CSM)	ed %	(ACME)	(CSM)	ed %	(ACME)	(CSM)	d %	(ACME)	(CSM)	ed %
M1 S1	111.0	53.5	48.2	2.0	1.9	94.9	60.4	39.2	64.9	48.1	44.1	91.7	13.7	22.7	165.3	51.8	84.7	163.5	1.4	1.0	74.0
M1 S2	40.0	27.1	67.7	1.0	3.4	334.7	19.6	11.5	58.5	50.6	44.2	87.4	14.6	17.0	116.4	52.2	68.8	131.8	0.2	1.2	586.4
M1 S3	37.0	23.1	62.5	3.0	4.5	150.8	25.4	14.9	58.7	59.2	47.7	80.6	13.5	15.4	114.0	49.5	60.3	121.8	1.1	1.3	119.9
M1 S3 Dupl	38.0	20.7	54.4	5.0	4.4	88.1	23.2	13.6	58.8	59.0	46.9	79.5	13.4	14.6	108.9	48.0	58.9	122.6	0.2	0.9	457.5
M1 S4	23.0	13.6	59.3	4.0	4.3	107.7	14.3	4.0	27.9	53.2	39.9	75.0	14.7	14.3	97.4	51.3	57.6	112.3	0.1	1.1	1090.3
M1 S5	185.0	131.3	71.0	3.0	2.9	97.2	27.6	14.0	50.7	54.1	42.2	78.1	14.7	15.8	107.7	53.7	61.6	114.7	0.7	1.1	161.3
M1 S6	116.0	73.8	63.6	6.0	4.2	69.3	39.4	22.0	55.9	54.3	43.5	80.2	14.4	15.2	105.2	49.4	59.3	120.0	0.8	1.0	127.8
M1 S6 Dupl	106.0	67.7	63.9	1.0	3.5	350.4	51.8	29.8	57.5	56.7	44.0	77.5	14.4	14.9	103.5	51.7	57.4	111.0	0.5	0.7	143.1
M1 S7	84.0	68.8	81.9	2.0	4.7	233.2	31.8	18.2	57.2	55.8	43.9	78.7	14.6	15.5	106.2	52.8	58.9	111.5	0.9	0.9	101.0
M1 58	53.0	31.1	58.7	4.0	5.7	141.3	30.0	16.9	56.2	54.2	40.7	75.0	14.8	14.3	96.4	53.7	59.2	110.2	0.1	0.7	682.8
M2 51	42.0	33.9	80.8	2.0	2.0	101.0	90.9	69.4	76.4	56.6	32.3	57.0	15.4	17.9	116.4	56.1	84.2	150.1	0.2	1.1	550.2
NIZ 52 M2 82	85.0	51.7	60.8	2.0	3.1	153.5	41.3	32.3	/8.2	55.5	39.4	71.1	16.7	15.4	92.5	57.3	74.7	130.4	0.6	0.7	112.2
M2 S2 Dupl	95.0	62.0	70.9	1.0	2.2	222.0	26.7	13.1	48.9	55.8	39.6	70.9	13.9	13.8	99.2	57.0	69.6	122.2	0.1	0.4	417.8
M2 S3 Dupi	92.0	63.9 E4.1	61.5	3.0	2.2	13.0	24.4	12.0	49.0	04.0 62.5	51.9	09.4	14.4	14.2	94.9	57.5	66.9	120.5	0.2	0.3	652.5
M2 54 M2 55	86.0	25.2	40.0	2.0	3.2	190.6	43.3	33.7	70.6	55 3	19.0	01.3	13.5	14.3	100.0	33.0 40.2	61.1	124.2	5.0	0.7	26.0
M2 55	85.0	63.6	74.8	4.0	3.5	69.8	J4.2 /1.5	34.5	83.2	47.9	40.0	90.7	15.4	14.0	97.6	49.3	72.2	124.0	0.1	0.2	166.4
M2 S7	67.0	/0.5	73.8	5.0	3.0	77.6	33.0	24.6	72.5	60.7	45.4	74.7	13.7	13.8	100.8	49.2	60.5	123.0	0.1	0.2	176.1
M2 S8	28.0	20.7	74.0	5.0	53	105.8	33.3	17.0	53.7	57.7	43.4	84.4	11.0	16.0	134.3	45.2	66.6	1/2 1	0.1	0.2	/3.2
M2 S8 Dupl	28.0	20.7	87.3	5.0	3.6	72.8	29.5	15.8	53.5	57.3	35.7	62.3	12.2	12.5	104.5	49.3	56.2	114 1	0.1	0.0	51.3
M2 S9	39.0	32.1	82.3	5.0	3.7	74.6	38.4	21.6	56.1	54.1	43.4	80.2	12.2	13.0	106.9	47.3	55.5	117.2	0.0	0.5	445.2
M2 S10	40.0	29.7	74.1	4.0	6.8	169.4	39.9	21.5	54.0	55.5	53.9	97.2	13.8	15.1	109.2	48.4	60.9	125.8	0.1	0.0	0.0
M3 S1	64.0	41.6	65.1	2.0	4.5	223.7	100.5	67.6	67.2	54.5	46.4	85.1	14.1	14.8	104.6	51.3	61.5	119.9	0.9	0.4	40.0
M3 S2	51.0	42.2	82.8	4.0	3.7	93.5	32.1	14.7	45.9	57.3	50.0	87.3	14.5	15.1	104.0	54.9	63.0	114.7	0.1	0.0	17.2
M3 S3	65.0	48.0	73.9	8.0	7.2	90.4	47.9	28.1	58.7	62.7	57.8	92.2	14.8	15.4	103.8	52.6	62.5	118.8	0.4	0.3	63.2
M3 S4	61.0	41.3	67.6	4.0	9.0	226.1	157.9	114.6	72.6	53.2	51.0	95.8	14.2	15.5	109.5	51.4	65.1	126.6	3.6	0.8	20.7
M3 S4 Dupl	60.0	49.9	83.2	10.0	9.8	98.3	143.7	130.4	90.8	52.9	57.3	108.3	13.3	18.8	141.4	49.4	89.5	181.2	3.1	0.5	15.1
M3 S5	95.0	62.6	65.9	6.0	6.1	101.4	76.4	54.7	71.6	57.8	48.2	83.4	14.0	14.7	105.1	49.2	67.4	136.9	0.8	0.2	30.5
M3 S6	72.0	42.8	59.5	6.0	4.1	67.5	71.9	51.0	70.9	57.8	39.3	67.9	13.4	13.9	104.0	50.7	62.1	122.5	2.5	0.3	13.7
M3 S7	34.0	19.1	56.3	4.0	4.6	113.9	13.5	4.5	33.5	63.5	46.8	73.7	13.8	14.1	102.3	50.7	62.5	123.2	0.1	0.0	0.0
M3 S8	182.0	97.0	53.3	6.0	6.2	103.7	75.4	46.7	61.9	52.1	49.8	95.6	11.7	13.4	114.1	41.4	54.7	132.1	13.0	2.5	19.6
M3 S9	166.0	115.6	69.6	5.0	6.3	124.9	47.3	36.6	77.4	52.6	52.4	99.6	11.7	10.6	90.3	43.2	55.6	128.7	12.4	3.8	30.5
M3 S9 Dupl	162.0	110.2	68.0	6.0	6.4	106.9	46.2	41.8	90.4	50.6	52.9	104.5	12.4	10.7	86.2	41.1	57.7	140.3	11.5	3.5	30.4
M4 S1	59.0	36.4	61.7	4.0	4.1	101.1	44.7	26.6	59.5	61.2	49.4	80.7	12.7	10.8	84.8	45.8	58.0	126.6	1.0	0.0	0.0
M4 S1 Dupl	58.0	29.4	50.6	2.0	3.8	188.4	36.9	20.7	56.2	61.7	44.4	72.0	13.1	9.7	74.2	46.0	54.4	118.3	1.1	0.0	0.0
M4 S2	41.0	24.4	59.5	4.0	3.3	82.3	25.1	9.4	37.4	60.6	39.5	65.1	12.2	8.6	70.6	45.1	52.3	115.9	0.9	0.0	0.0
M4 S3	51.0	39.4	77.2	4.0	3.7	91.7	20.6	7.5	36.4	54.7	50.1	91.6	12.6	11.5	91.0	46.1	61.3	132.9	0.1	0.0	0.0
M4 S4	29.0	19.9	68.5	4.0	3.8	95.4	20.2	6.8	33.8	61.1	48.8	79.8	13.7	11.6	84.8	51.9	61.9	119.2	0.2	0.0	0.0
M4 S5	/1.0	32.0	45.1	6.0	4.9	81.6	45.4	17.6	38.8	58.7	50.1	85.3	13.3	11.4	86.0	46.7	61.8	132.3	5.4	0.9	15.9
M4 S6	52.0	44.4	85.3	2.0	2.2	111.9	18.6	6.3	34.0	57.5	49.5	86.1	12.5	11.4	91.1	47.4	61.5	129.8	0.2	0.0	0.0
M4 S7	58.0	45.6	78.5	1.0	2.5	246.8	24.2	10.0	41.4	57.3	53.1	92.6	13.5	11.1	82.3	48.8	60.1	123.1	0.2	0.0	0.0
NI4 58	83.0	60.8	73.3	2.0	3.3	164.7	21.6	11.0	50.8	59.5	47.3	79.5	13.1	11.7	89.3	49.3	61.0	123.7	0.3	0.0	0.0
W14 59 M4 610	31.0	30.2	97.3	3.0	3.5	79.0	47.2	34.0	/2.1	6Z.4	30.3	58.2	14.6	15.1	103.2	54.2	90.5	167.0	0.1	0.0	0.0
M4 S10	40.0	32.4	70.5	3.0	2.4	10.2	9.00	20.9	31.2	57.1	23.2	40.7	15.7	0.1	40.1	1.00	51.3	91.4	0.5	0.0	0.0
Dupl	45.0	24.9	55.4	3.0	4.6	151.9	56.4	35.2	62.4	58.3	61.5	105.5	15.9	13.3	83.4	55.5	76.0	137.0	0.6	0.0	0.0
Average	/1.2	47.3	67.8	3.8	4.4	133.3	45.8	29.2	58.1	56.6	45.8	81.4	13.8	13.9	101.0	50.6	63.9	126.5	1.6	0.6	147.9

Note: The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results represent the total amount of each element in the sample.

Sample Name	Sr (ACME)	Sr (CSM)	Dissolved	Ta (ACME)	Ta (CSM)	Dissolved	Th (ACME)	Th	Dissolved		U (CSM)	Dissolved		V (CSM)	Dissolved	W (ACME)	W (CSM)	Dissolved	Zr (ACME)	Zr	Dissolved
M1 S1	(ACIVIE)	(CSIVI) 86.7	70		(0.311)	70		(CSIVI) 45.5	70	(ACIVIE)	(0.5101)	70		(CSIVI) 352.0	76 2		291.6	101.0	(ACIVIE)	(CONI) 549.1	106.7
M1 S2	240.2	11 1	44.0	4.0	28.5	678.9	60.7	46.5	76.5	5.0	4.9	98.3	347.0	284.4	82.0	112.6	253.8	225.4	500.8	558.7	111.6
M1 S3	21.4	6.0	27.9	3.8	17.9	471.4	48.1	21.3	44.3	4.8	4.4	92.2	360.0	275.5	76.5	59.6	193.5	324.7	477.2	534.9	112.1
M1 S3 Dupl	21.6	5.9	27.4	4.0	15.2	381.1	46.7	17.5	37.4	5.4	4.1	76.5	334.0	261.9	78.4	69.7	195.3	280.2	479.3	511.4	106.7
M1 S4	27.2	7.8	28.8	3.7	14.6	395.7	53.8	18.5	34.4	5.2	4.1	79.0	373.0	265.8	71.3	61.6	182.4	296.1	518.6	509.3	98.2
M1 S5	26.8	10.8	40.3	5.0	13.0	260.1	57.2	30.0	52.5	6.3	5.6	88.2	250.0	195.0	78.0	126.7	239.1	188.7	526.9	575.8	109.3
M1 S6	23.9	10.4	43.5	4.7	13.3	283.0	54.0	28.0	51.9	5.0	4.5	90.4	324.0	261.2	80.6	92.2	209.5	227.2	505.5	545.5	107.9
M1 S6 Dupl	23.9	8.4	35.3	4.5	11.1	245.6	53.2	23.8	44.8	5.4	4.3	79.3	345.0	244.5	70.9	129.5	250.5	193.4	508.4	538.5	105.9
M1 S7	21.6	12.4	57.3	4.1	10.9	266.0	54.5	31.3	57.4	5.7	5.0	88.4	433.0	365.7	84.5	98.5	202.5	205.6	537.3	562.1	104.6
M1 S8	20.9	7.2	34.5	4.5	10.8	239.2	55.5	19.9	35.9	5.8	4.6	79.5	410.0	319.5	77.9	118.7	235.3	198.2	520.0	517.9	99.6
M2 S1	52.2	32.8	62.8	4.4	30.9	701.4	53.7	36.8	68.5	10.1	8.3	82.2	747.0	447.3	59.9	81.5	197.4	242.2	541.5	540.9	99.9
M2 S2	42.7	21.9	51.2	5.2	20.1	386.1	54.3	26.8	49.3	9.2	7.6	82.2	630.0	552.3	87.7	125.6	253.3	201.7	584.2	558.8	95.6
M2 S3	31.0	9.9	32.0	4.5	12.4	274.9	41.8	14.5	34.7	7.3	5.5	75.5	585.0	464.8	79.4	167.9	280.3	167.0	501.8	516.8	103.0
M2 S3 Dupi	32.0	11.2	34.9	4.7	11.7	249.4	42.2	14.0	33.2	7.2	5.5	76.8	601.0	486.3	80.9	158.5	285.6	180.2	517.2	515.5	99.7
M2 54	44.5	16.4	36.9	4.4	12.3	280.4	46.1	18.6	40.4	7.6	6.7	88.7	562.0	4/3.6	84.3	103.2	229.8	222.7	490.1	530.4	108.2
M2 55	48.1	14.7	30.5	5.3	11.7	220.3	47.1	20.1	42.8	7.6	0.4	84.3	826.0	802.5	97.2	1/6.5	311.4	176.4	492.6	549.4	111.5
M2 30 M2 57	23.0	10.0	75.0	3.1	12.2	230.0	50.0	40.9	51 1	10.3	9.0	91.0	705.0	/11.2	91.0	147.3	201.0	175.4	401.0	530.3	103.5
M2 57	22.2	10.0	33.1	4.5	3.3	500.0	45.1	20.0	51.1	0.0	6.8	92.5	400.0 616.0	562.6	00.3	1/2.5	262.4	195.9	491.9	527.7	117.2
M2 S8 Dunl	24.4	13.0	44.0	3.8	11.8	311.7	45.1	20.7	43.2	8.2	6.3	76.7	668.0	600.8	90.0	123.0	198.3	161.3	463.0	482.6	104.2
M2 S9	20.2	9.9	49.0	3.9	11.0	299.2	51.0	29.1	57.1	9.4	7 1	75.2	707.0	637.8	90.2	164.3	255.6	155.6	427.2	502.8	117.7
M2 S10	22.8	9.8	42.8	4.4	11.3	257.7	53.3	36.9	69.2	9.6	7.4	77.2	724.0	671.6	92.8	168.0	299.3	178.2	505.0	593.5	117.5
M3 S1	38.6	14.8	38.4	4.7	9.6	203.8	57.8	29.6	51.3	8.7	6.9	79.6	1021.0	872.5	85.5	120.8	249.8	206.8	495.4	563.2	113.7
M3 S2	45.4	21.6	47.6	4.0	9.4	234.2	56.8	35.9	63.2	11.5	8.6	74.9	1112.0	1030.8	92.7	75.5	193.7	256.5	546.2	591.2	108.3
M3 S3	33.5	14.4	42.9	4.6	9.1	197.2	52.6	34.0	64.6	14.2	11.5	80.6	1186.0	1102.7	93.0	113.2	242.5	214.2	518.4	604.5	116.6
M3 S4	43.3	19.9	46.0	4.1	8.9	217.9	48.3	29.5	61.1	11.4	9.5	82.9	835.0	700.5	83.9	57.7	184.9	320.5	500.5	604.9	120.9
M3 S4 Dupl	43.5	26.6	61.2	4.6	32.0	695.5	45.8	41.6	90.9	11.1	10.3	92.8	765.0	786.3	102.8	55.2	180.4	326.9	500.8	617.6	123.3
M3 S5	41.7	16.1	38.6	4.2	15.6	370.2	52.6	25.8	49.0	12.0	9.6	79.9	933.0	852.8	91.4	133.2	258.7	194.2	497.5	570.1	114.6
M3 S6	67.3	29.7	44.1	4.4	11.1	252.8	60.9	27.4	45.1	11.5	9.1	79.3	897.0	682.2	76.1	61.9	182.6	294.9	487.4	553.5	113.6
M3 S7	64.8	16.0	24.7	4.0	9.5	236.7	59.3	18.6	31.3	10.1	7.7	75.8	1015.0	865.4	85.3	50.4	173.1	343.4	508.4	553.9	109.0
M3 S8	80.2	33.8	42.1	3.7	8.3	225.0	56.5	23.9	42.3	7.7	4.3	56.1	996.0	905.6	90.9	83.5	212.5	254.5	421.0	528.9	125.6
M3 S9	68.8	31.7	46.0	3.4	9.1	266.4	53.1	33.5	63.1	8.0	6.9	86.1	821.0	813.8	99.1	61.8	111.4	180.3	427.6	409.4	95.8
M3 59 Dupi	67.8	30.0	44.3	3.5	9.4	268.5	54.4	32.6	60.0	8.3	7.3	87.5	786.0	790.6	100.6	47.9	/5.1	156.8	418.2	411.1	98.3
M4 S1	31.8	11.4	35.7	4.4	8.2	186.4	45.6	19.2	42.0	5.9	4.6	77.1	444.0	402.6	90.7	154.2	169.0	109.6	442.9	414.5	93.6
M4 S1 Dupi	34.3	13.8	40.1	3.9	8.1	206.8	41.7	20.5	49.1	6.0	4.7	77.5	434.0	355.3	81.9	84.1	97.7	116.2	449.4	386.6	86.0
M4 52	26.4	12.2	20.5	3.9	0.0	168.5	41.4	28.0	28.9	5.8	3.5	60.0	420.0	334.9	79.7	84.7	88.7 00 E	104.7	442.8	326.4	73.7
M4 55 M4 54	22.0	12.2	33.7	3.0	0.0	220.0	45.2	20.9	59.5	5.2	3.9	63.4	408.0 531.0	407.4 514.0	99.9	74.0	68.8	100.3	404.4	435.9	95.9
M4 S5	50.5	14.5	28.5	3.5	9.0 7.4	229.9	17.9	25.3	52.3	6.8	3.0	50.2	492.0	/3/ 7	88.4	/4.0	10.0	100.1	491.5	44J.7 /37.3	90.7
M4 05	22.2	10.3	46.4	4.1	83	200.1	48.4	29.3	60.5	5.2	3.8	72.8	408.0	413.1	101.2	88.7	86.9	98.0	460.7	425.1	92.3
M4 S7	26.0	11.0	42.4	4.3	8.0	185.5	54 1	33.9	62.7	5.1	3.8	75.0	590.0	552.9	93.7	120.6	115.6	95.8	495.6	436.3	88.0
M4 S8	32.3	11.0	34.2	4.1	7.1	174.3	52.3	25.1	48.0	6.0	4.9	81 7	670.0	600.7	89 7	95.1	107.5	113.0	499.0	454.4	91.1
M4 S9	33.7	24.7	73.3	4,1	33.8	825.3	47.7	23.7	49.6	6.5	5.1	78.4	585.0	589.4	100.8	74.0	61.3	82.8	518.4	420.7	81.2
M4 S10	40.1	15.9	39.6	4.9	10.5	213.6	50.0	12.8	25.6	7.0	3.9	55.8	552.0	413.4	74.9	132.7	57.3	43.2	566.9	280.6	49.5
M4 S10 Dupl	39.3	12.2	31.1	5.0	11.6	232.8	48.0	31.2	64.9	7.3	5.3	72.7	534.0	523.4	98.0	100.3	113.6	113.2	549.2	514.6	93.7
Average	40.8	17.0	41.6	4.3	13.9	324.6	51.2	27.2	52.7	7.7	6.1	78.7	620.4	545.1	86.8	105.5	190.4	188.8	495.6	507.5	102.6

Table 10.8b. Trace element recoveries (ppm) of bauxite samples prepared using lithium borate fusion – dissolution procedure in comparison with the 4 acids attack.

Note: The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results represent the total amount of each element in the sample.

Table 10.8c. REE recovery valu	les (ppm) of bauxite sa	amples prepared usin	g the lithium borate fus	ion – dissolution procedure	in comparison
with the 4 acids attack.					

Samplo Namo	La	La	Dissolved	Ce	Ce	Dissolved	Pr	Pr	Dissolved	Nd	Nd	Dissolved	Sm	Sm	Dissolved	Eu	Eu	Dissolved	Gd	Gd	Dissolved	Tb	Tb	Dissolved
Sample Name	(ACME)	(CSM)	%																					
M1 S1	26.7	2.2	8.0	404.2	39.4	9.8	13.0	1.5	11.3	55.8	6.8	12.3	13.9	2.0	14.2	3.0	0.5	14.8	12.9	1.7	13.1	1.8	0.2	10.5
M1 S2	9.6	1.5	16.1	120.9	26.8	22.2	2.4	0.8	35.3	7.9	2.2	28.0	2.0	0.9	46.5	0.5	0.6	107.7	3.2	1.2	37.0	0.7	0.6	87.7
M1 S3	10.6	0.6	5.9	84.9	4.0	4.7	2.1	0.5	21.2	7.7	0.7	8.5	1.7	0.4	25.6	0.5	0.4	87.9	2.6	0.5	19.9	0.6	0.4	56.2
M1 S3 Dupl	10.4	0.6	5.6	87.5	2.9	3.3	2.2	0.4	18.9	7.6	0.6	8.5	1.8	0.4	23.2	0.4	0.4	94.3	2.5	0.5	17.7	0.6	0.4	64.4
M1 S4	18.9	0.8	4.0	96.2	4.0	4.2	3.5	0.5	15.4	11.6	0.9	7.9	2.2	0.5	23.2	0.6	0.5	87.1	3.2	0.6	18.7	0.7	0.5	66.8
M1 S5	10.6	1.5	14.4	171.8	22.5	13.1	2.7	0.8	29.7	10.5	2.0	19.0	2.2	0.9	38.4	0.6	0.6	101.3	3.7	1.0	25.8	0.7	0.6	87.6
M1 S6	8.1	1.3	15.7	175.7	28.2	16.0	2.2	0.7	31.7	7.9	1.7	21.8	2.0	0.8	41.0	0.5	0.5	94.0	3.4	1.0	29.5	0.7	0.5	65.3
M1 S6 Dupl	8.4	0.9	11.1	186.6	18.2	9.7	2.3	0.6	26.0	8.7	1.2	14.2	2.1	0.7	30.4	0.5	0.5	94.8	3.5	0.8	23.2	0.7	0.5	69.4
M1 S7	28.2	11.7	41.6	273.9	113.3	41.4	7.1	3.5	49.1	25.5	12.2	47.9	5.2	3.0	57.0	1.2	1.0	81.6	6.4	2.9	45.3	1.1	0.9	77.9
M1 S8	21.9	1.0	4.7	348.8	19.6	5.6	4.7	0.6	12.2	17.0	1.4	8.1	3.4	0.6	17.2	0.8	0.4	48.5	5.4	0.6	11.8	0.9	0.4	41.0
M2 S1	16.2	3.0	18.4	140.0	36.1	25.8	3.4	1.3	38.8	13.4	3.9	29.3	3.0	1.4	47.3	0.7	0.7	92.1	4.2	1.5	35.9	0.9	0.7	76.6
M2 S2	16.9	1.3	7.6	194.8	20.9	10.7	3.4	0.7	20.7	12.2	1.6	13.4	2.9	0.8	25.9	0.6	0.5	82.4	4.0	0.8	20.1	0.8	0.5	61.1
M2 S3	11.9	0.4	3.1	197.2	10.7	5.4	3.3	0.2	5.1	12.0	0.7	6.0	3.1	0.2	7.9	0.8	0.1	10.3	4.6	0.3	5.7	0.9	0.0	0.0
M2 S3 Dupi	11.8	0.5	4.6	188.8	11.8	6.2	3.2	0.3	9.3	12.6	0.9	7.2	3.3	0.4	10.9	0.8	0.2	23.2	4.4	0.5	10.1	0.9	0.1	13.7
N2 54	15.5	1.0	0.1	186.7	12.9	6.9	5.9	0.7	12.3	22.5	1.0	7.8	5.2	0.8	15.3	1.2	0.5	43.4	5.4	0.9	15.6	1.0	0.5	40.8
N2 55	159.0	3.9	2.5	1/6./	11.7	0.0	20.6	1.1	5.3	36.1	3.0	5.3	9.9	1.0	9.7	2.2	0.5	23.1	9.5	1.0	11.0	1.7	0.5	27.0
M2 S7	20.0	12.5	21.2	364.6	100.7	39.1	6.7	3.7	31.0	40.7	14.5	30.0	8.0	3.2	39.6	1.7	0.7	41.0	9.5	3.1	33.2	1.4	0.5	33.0
M2 57	20.3	3.9	13.0	407.0	109.7	23.3	0.7	1.4	20.1	24.2	5.5	22.0	5.2	1.2	24.0	1.2	0.3	24.4	7.0	1.3	19.1	1.0	0.2	10.0
M2 S8 Dupl	30.3	3.3	9.0	240.9	30.1	10.0	0.7	1.2	15.0	32.1	4.9	10.3	0.9	1.2	17.2	1.5	0.3	19.0	0.1	1.2	14.0	1.2	0.1	22.0
M2 30 Dupi	30.0	10.0	40.0	193.2	59.5	32.7	9.0	4.3	40.0	22.9	7.4	43.3	5.3	3.0	49.4	1.0	0.6	40.0	5.0	3.1	40.9	1.3	0.4	33.9
M2 S10	20.3	6.2	15.8	282.6	91.6	32.4	10.0	2.0	29.9	25.0	8.5	24.0	3.3	2.0	27.5	1.2	0.5	28.1	7.9	2.0	25.1	1.1	0.4	24.5
M3 S1	18.2	2.2	12.0	598.2	111.8	18.7	6.4	1 1	17.3	23.8	0.5	18.6	6.0	1.3	20.9	1.0	0.3	20.1	7.0	1.0	17.0	1.5	0.4	17.0
M3 S2	35.1	7.7	22.0	179.2	59.6	33.2	6.3	1.1	28.3	20.5	6.3	30.7	43	1.5	20.9	1.5	0.3	35.0	5.2	1.2	30.0	1.1	0.2	26.3
M3 S3	38.4	5.1	13.3	260.9	71.3	27.3	7.0	1.0	19.7	23.8	4.8	20.0	5.4	1.0	26.7	1.0	0.4	29.3	6.7	1.0	22.0	1.0	0.0	23.7
M3 S4	122.4	12.3	10.0	138.9	25.1	18.1	20.4	3.3	16.0	65.1	11.2	17.2	15.1	31	20.7	37	0.9	24.9	17.2	3.5	20.5	3.7	0.9	24.6
M3 S4 Dupl	113.8	25.5	22.4	146.8	47.5	32.4	19.2	6.0	31.4	63.4	20.9	33.0	14.6	5.5	37.9	3.6	1.3	36.5	16.2	5.8	35.5	3.5	1.3	36.7
M3 S5	56.9	4.2	7.4	238.5	25.0	10.5	11.8	1.4	11.5	39.4	4.7	11.9	9.5	1.4	14.4	2.3	0.4	18.8	10.4	1.3	12.2	2.1	0.4	16.6
M3 S6	24.1	1.9	7.9	149.8	16.1	10.7	5.0	0.7	13.0	16.9	2.4	14.1	3.4	0.7	19.2	0.8	0.2	21.4	4.3	0.7	15.0	0.8	0.1	6.2
M3 S7	36.5	0.7	1.9	192.2	6.1	3.2	8.0	0.3	3.6	26.4	0.8	3.2	4.3	0.3	6.3	0.9	0.1	10.7	4.9	0.3	5.4	0.9	0.0	1.8
M3 S8	54.8	2.4	4.4	184.9	17.2	9.3	11.7	1.0	8.4	38.2	3.4	9.0	7.3	1.0	14.3	1.8	0.4	19.9	7.8	1.1	13.4	1.7	0.4	22.9
M3 S9	57.7	4.8	8.4	154.3	29.4	19.1	11.1	1.7	15.0	35.8	6.1	17.0	7.1	1.6	22.0	1.6	0.4	24.9	7.8	1.7	21.5	1.5	0.3	22.6
M3 S9 Dupl	53.4	3.0	5.7	149.2	22.6	15.2	10.6	1.2	11.4	35.9	4.5	12.5	7.2	1.4	18.9	1.6	0.4	26.8	7.4	1.3	17.9	1.5	0.4	29.5
M4 S1	9.9	0.5	4.8	112.8	8.1	7.2	2.6	0.3	9.6	10.6	0.8	7.8	2.6	0.4	14.0	0.6	0.1	20.5	3.6	0.4	11.4	0.7	0.1	10.7
M4 S1 Dupl	10.4	0.8	7.4	123.4	18.9	15.3	2.7	0.4	13.9	10.5	1.5	13.8	2.9	0.4	15.2	0.7	0.2	27.9	3.7	0.6	16.6	0.7	0.1	12.3
M4 S2	9.0	0.3	3.2	162.0	8.1	5.0	2.4	0.2	6.4	9.8	0.5	5.2	2.3	0.2	10.2	0.5	0.1	17.0	3.2	0.2	6.1	0.7	0.0	1.9
M4 S3	8.8	1.0	11.4	151.7	27.8	18.4	2.6	0.4	16.9	9.7	1.9	19.6	2.5	0.5	19.8	0.6	0.1	19.6	3.5	0.6	17.2	0.6	0.0	1.1
M4 S4	28.7	6.0	21.0	176.6	49.6	28.1	5.6	1.5	27.4	19.2	5.5	28.5	3.5	1.2	33.1	0.8	0.3	30.6	4.8	1.1	23.4	0.9	0.2	16.1
M4 S5	61.0	2.7	4.3	341.2	62.8	18.4	13.9	1.1	8.1	49.1	4.6	9.3	10.2	1.3	13.0	2.3	0.3	13.6	10.5	1.2	11.6	1.6	0.1	6.6
M4 S6	6.7	1.0	15.5	121.9	27.9	22.9	1.8	0.4	21.0	6.6	1.5	23.3	1.7	0.4	23.4	0.5	0.1	20.7	3.0	0.6	18.4	0.6	0.0	4.6
M4 S7	13.4	2.2	16.6	307.5	87.3	28.4	3.6	0.8	22.8	12.0	3.0	25.1	2.8	0.8	27.6	0.7	0.2	25.3	4.7	0.9	18.5	0.8	0.1	8.9
M4 S8	15.7	1.2	7.5	130.0	12.8	9.9	3.2	0.4	10.9	11.3	1.4	12.2	2.4	0.4	14.4	0.6	0.1	13.9	3.8	0.5	12.2	0.8	0.0	0.0
M4 S9	24.7	14.2	57.3	289.1	86.8	30.0	4.3	3.0	69.5	14.7	10.6	72.1	3.4	2.4	69.8	0.8	0.6	76.8	5.0	2.7	52.6	0.9	0.6	63.1
WI4 S10	32.8	6.0	18.2	511.1	65.7	12.9	5.9	1.6	26.5	21.8	5.5	25.4	4.4	1.3	29.0	1.1	0.3	31.2	1.2	1.4	20.0	1.1	0.3	22.9
WI4 STU DUPI	31.0	2.7	8.7	427.9	1/4.8	40.9	5.6	0.8	14.2	19.7	3.1	15.5	4.2	0.8	18.9	1.0	0.2	24.1	6.7	1.1	15.6	1.0	0.1	13.2
Average	32.8	4.2	13.0	224.4	43.9	17.8	6.8	1.3	20.6	23.7	4.6	19.2	5.2	1.3	25.7	1.2	0.4	41./	6.2	1.3	20.9	1.1	0.3	31.0

Note: The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results

represent the total amount of each element in the sample.

# Table 10.8d. REE recovery values (ppm) of bauxite samples prepared using the lithium borate fusion – dissolution procedure in comparison with the 4 acids attack.

Sample Name	Dy (ACME)	Dy (CSM)	Dissolve	Ho (ACME)	Ho (CSM)	Dissolve	Er (ACME)	Er (CSM)	Dissolve	Tm (ACME)	Tm (CSM)	Dissolve	Yb (ACME)	Yb (CSM)	Dissolve			Dissolve	Y (ACME)	Y (CSM)	Dissolve
M1 S1	97	1.8	18.4	1.9	0.4	19.5	5.0	11	22.4	0.8	0.2	23.4	52	1.3	24.2	0.7	0.2	26.3	44.6	55	12.2
M1 S2	5.1	2.0	39.0	1.1	0.8	72.5	3.7	1.6	44.8	0.6	0.7	112.8	4.1	1.8	45.0	0.7	0.7	103.1	30.8	6.8	21.9
M1 S3	4.8	0.8	16.3	1.1	0.4	41.7	3.7	0.7	19.7	0.6	0.4	72.1	4.3	0.9	19.8	0.7	0.4	63.7	31.4	2.3	7.2
M1 S3 Dupl	4.5	0.6	13.4	1.0	0.4	42.4	3.6	0.7	18.0	0.6	0.4	68.8	4.2	0.7	17.6	0.7	0.4	61.6	32.5	1.8	5.5
M1 S4	5.8	0.8	14.1	1.4	0.5	38.5	4.6	0.8	17.8	0.8	0.5	65.1	5.3	1.0	18.6	0.9	0.5	60.7	37.8	2.2	5.8
M1 S5	5.4	1.5	27.5	1.3	0.7	55.0	3.8	1.3	33.2	0.6	0.6	94.6	4.1	1.4	34.8	0.7	0.6	89.7	34.6	5.4	15.6
M1 S6	4.9	1.6	33.5	1.1	0.6	60.3	3.4	1.4	40.0	0.6	0.5	90.0	3.7	1.5	39.7	0.6	0.5	86.9	32.0	6.1	19.2
M1 S6 Dupl	5.1	1.1	21.6	1.2	0.6	52.3	3.6	1.0	28.7	0.6	0.5	87.6	3.8	1.1	29.4	0.6	0.5	88.3	34.1	3.5	10.4
M1 S7	7.3	4.0	53.9	1.6	1.2	71.6	5.1	3.0	58.3	0.8	0.8	91.1	5.5	3.1	56.4	0.9	0.8	93.1	44.3	18.1	40.7
M1 S8	6.7	1.1	15.7	1.6	0.5	31.5	5.1	1.0	19.5	0.8	0.4	52.9	5.7	1.1	19.1	0.9	0.5	54.7	43.0	2.9	6.7
M2 S1	6.4	2.1	32.5	1.4	0.8	60.1	4.3	1./	38.5	0.6	0.7	107.6	4.4	1.8	42.2	0.7	0.7	97.4	40.7	7.8	19.1
NIZ 52 M2 52	5.6	1.2	21.9	1.2	0.6	48.8	4.0	1.1	20.5	0.6	0.5	89.2	4.1	1.2	28.6	0.7	0.5	15.3	34.4	3.5	10.2
M2 S2 Dupl	0.1	0.0	10.1	1.4	0.2	10.5	4.3	0.5	11.0	0.7	0.1	14.1	4.7	0.0	12.9	0.7	0.1	15.0	37.4	2.3	0.1
M2 S3 Dupi M2 S4	6.9	0.9	14.0	1.3	0.3	20.7	4.1	0.7	17.1	0.6	0.2	33.0	4.4	0.8	10.3	0.7	0.2	31.3	37.3	2.7	7.Z 9.1
M2 S5	10.6	1.2	14.5	2.1	0.0	28.9	5.9	1.0	19.8	1.0	0.5	50.5	6.8	1.1	22.2	1 1	0.5	48.8	45.4	3.0	8.2
M2 S6	9.2	3.9	42.5	19	0.0	41.5	5.4	2.4	44.5	0.9	0.0	42.1	5.8	2.4	42.0	0.9	0.0	41.9	53.2	14.9	28.1
M2 S7	6.8	1.9	27.8	1.4	0.4	27.9	4.5	1.3	29.5	0.7	0.2	28.4	4.9	1.4	28.6	0.8	0.2	28.2	39.5	7.0	17.7
M2 S8	8.3	1.7	20.9	1.7	0.4	21.6	5.0	1.2	24.1	0.8	0.2	23.1	5.6	1.5	26.5	0.9	0.2	22.9	43.8	6.5	14.7
M2 S8 Dupl	8.2	3.6	43.7	1.8	0.8	43.2	5.1	2.5	48.8	0.9	0.4	43.7	5.6	2.5	45.3	0.9	0.4	43.6	46.3	17.3	37.3
M2 S9	7.1	2.9	40.9	1.5	0.7	43.3	4.9	2.0	40.4	0.8	0.4	51.6	5.6	2.4	43.1	0.9	0.4	49.4	42.1	11.8	28.1
M2 S10	9.7	3.0	31.4	2.0	0.7	33.8	6.1	2.2	36.4	1.1	0.4	38.5	7.8	2.8	35.3	1.1	0.4	37.6	52.6	12.0	22.7
M3 S1	6.4	1.5	23.2	1.4	0.4	30.1	4.1	1.1	25.9	0.7	0.2	30.2	4.5	1.2	25.7	0.7	0.2	29.5	36.7	5.9	16.0
M3 S2	7.4	2.8	38.1	1.7	0.7	38.6	5.1	2.1	41.3	0.9	0.4	39.7	5.9	2.5	41.7	0.9	0.4	40.3	43.1	13.5	31.4
M3 S3	9.0	2.7	30.0	2.0	0.6	31.7	6.1	2.0	32.2	1.0	0.4	36.1	7.2	2.3	31.8	1.1	0.4	34.1	49.1	10.2	20.9
M3 S4	23.8	6.3	26.3	4.6	1.3	28.3	12.9	3.7	29.1	2.0	0.7	34.8	14.0	4.6	32.7	2.2	0.8	36.5	63.8	11.2	17.5
M3 S4 Dupl	23.3	9.5	40.8	4.2	1.8	43.2	12.2	5.5	44.7	1.9	0.9	46.0	13.4	6.3	47.2	2.1	1.0	46.8	60.1	19.0	31.7
M3 S5	14.7	2.4	16.5	3.0	0.6	20.2	8.9	1./	19.0	1.5	0.4	28.7	10.1	2.1	20.9	1.6	0.4	26.3	54.7	5.5	10.1
N3 50	5.9	1.1	18.9	1.3	0.3	22.4	4.1	0.9	21.9	0.7	0.2	25.3	4.8	1.1	22.3	0.7	0.2	25.6	36.8	4.3	11.7
N3 57	0.0	0.4	0.0	1.4	0.2	11.4	4.8	0.5	9.4	0.8	0.1	14.1	5.7	0.5	0.9	0.9	0.1	14.5	30.4	1.0	4.0
M3 S9	10.0	2.9	27.5	2.3	0.5	23.5	0.9	1.0	23.1	1.1	0.4	35.0	0.3	1.0	22.1	1.3	0.3	37.0	49.1	0.0 0.4	11.0
M3 S9 Dupl	10.4	2.3	27.5	2.2	0.7	28.1	6.8	1.7	24.9	1.1	0.4	37.2	7.0	2.0	27.7	1.2	0.4	38.5	49.7	6.7	13.7
M4 S1	4.8	0.8	15.9	11	0.0	20.1	3.6	0.6	16.9	0.6	0.4	28.8	3.9	0.7	18.1	0.6	0.4	29.2	31.8	2.6	81
M4 S1 Dupl	4.8	0.9	19.6	1.1	0.3	23.1	3.2	0.7	22.4	0.6	0.2	29.3	3.9	0.9	22.0	0.6	0.2	27.6	31.1	3.5	11.4
M4 S2	4.6	0.4	9.0	1.0	0.1	12.7	3.2	0.3	10.1	0.5	0.1	19.5	3.6	0.4	12.0	0.6	0.1	21.6	29.0	1.4	4.8
M4 S3	4.5	1.1	24.0	1.0	0.2	23.2	3.3	0.8	24.4	0.5	0.1	26.1	3.6	1.0	27.4	0.6	0.2	28.2	28.0	4.1	14.7
M4 S4	6.8	2.3	33.1	1.6	0.5	32.8	5.2	1.9	35.8	0.9	0.3	32.9	6.1	2.1	33.6	0.9	0.3	32.5	44.6	10.6	23.8
M4 S5	10.8	1.7	15.9	2.2	0.4	17.2	6.8	1.3	19.9	1.1	0.2	18.9	7.4	1.7	22.3	1.1	0.3	22.4	54.4	6.5	12.0
M4 S6	4.5	1.2	25.8	1.0	0.3	28.2	3.2	1.0	31.2	0.5	0.2	29.9	3.5	1.1	32.5	0.6	0.2	31.4	28.4	5.8	20.4
M4 S7	5.4	1.6	29.1	1.3	0.3	27.3	4.0	1.2	30.5	0.7	0.2	29.1	4.5	1.4	32.0	0.7	0.2	30.1	36.1	7.2	19.9
M4 S8	5.8	1.0	17.5	1.4	0.2	16.6	4.4	0.8	19.1	0.7	0.1	20.7	4.9	1.0	19.9	0.8	0.2	21.7	38.8	4.3	11.2
M4 S9	6.7	4.4	65.7	1.6	1.1	71.5	5.2	3.5	66.7	0.9	0.6	70.3	5.8	3.7	63.5	0.9	0.6	73.4	46.0	27.9	60.7
M4 S10	7.5	2.0	26.7	1.7	0.5	28.8	5.6	1.6	29.2	0.8	0.3	36.9	6.1	1.8	30.2	0.9	0.3	33.9	49.3	9.5	19.3
M4 S10 Dupl	7.7	1.6	21.1	1.7	0.4	23.6	5.2	1.3	25.5	0.9	0.3	28.5	5.9	1.6	26.5	0.9	0.3	28.6	47.7	7.4	15.6
Average	7.8	2.1	25.4	1.7	0.6	34.2	5.1	1.5	28.9	0.8	0.4	46.3	5.8	1.7	29.4	0.9	0.4	45.2	41.6	7.4	16.9

Note: The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results represent the total amount of each element in the sample.

Table 10.8e. Rest of trace elements values (ppm) of bauxite samples prepared using the lithium borate fusion – dissolution procedure or the 4 acids attack.

Sample Name	Cs (ACME)	Sn (ACME)	Ag (CSM)	As (CSM)	Bi (CSM)	Cd (CSM)	Cr (CSM)	Cu (CSM)	Ge (CSM)	Mo (CSM)	Ni (CSM)	Pb (CSM)	Sb (CSM)	Sc (CSM)	Zn (CSM)
M1 S1	0.3	11.0	0.3	42.5	4.3	0.0	958.9	6.3	5.3	29.3	606.7	4.9	18.7	38.8	35.2
M1 S2	0.1	11.0	0.7	57.9	4.2	0.0	1154.8	4.2	4.5	18.8	184.9	31.4	16.2	33.8	8.9
M1 S3	0.1	11.0	0.6	52.2	2.9	0.1	969.7	5.1	15.9	10.7	197.7	23.5	10.3	22.3	6.8
M1 S3 Dupl	0.1	11.0	0.6	49.9	2.4	0.2	936.1	6.7	18.1	8.2	179.8	23.2	9.4	21.2	14.0
M1 S4	0.1	12.0	0.6	34.0	2.3	0.5	834.2	3.5	7.2	6.1	158.2	20.0	9.3	25.1	5.8
M1 S5	0.1	13.0	0.6	380.1	2.8	0.0	1021.8	3.7	24.5	27.7	187.5	15.9	7.4	29.6	3.8
M1 S6	0.2	12.0	0.5	56.2	2.6	0.0	929.4	4.7	5.9	6.9	233.8	13.2	7.5	38.2	4.5
M1 S6 Dupl	0.1	11.0	0.6	53.4	2.5	0.0	954.1	102.5	6.3	6.6	211.1	15.3	7.1	29.9	3.8
M1 S7	0.4	12.0	0.5	45.6	2.4	0.0	825.2	6.6	6.3	4.5	307.4	34.5	7.9	29.3	12.2
M1 S8	0.1	12.0	0.5	47.1	2.4	0.0	981.6	4.6	4.9	4.3	309.6	34.2	8.6	31.8	18.9
M2 S1	0.1	13.0	0.7	424.1	3.1	0.0	682.0	21.7	4.1	88.1	822.3	21.8	43.3	45.6	41.2
M2 S2	0.1	12.0	0.6	114.7	2.6	0.0	697.4	13.6	5.5	16.3	411.8	16.2	24.5	49.7	20.2
M2 S3	0.1	12.0	0.1	110.7	1.5	0.0	590.2	7.1	7.1	12.0	134.2	11.9	14.6	25.7	9.8
M2 S3 Dupl	0.1	12.0	0.2	123.0	1.5	0.0	609.1	8.1	8.5	11.6	148.4	13.8	15.1	29.3	10.9
M2 S4	0.1	11.0	0.5	139.0	2.1	0.0	686.4	34.5	6.4	8.6	320.8	16.9	17.2	39.3	27.3
M2 S5	1.0	11.0	0.5	87.3	2.2	0.0	736.7	142.4	10.3	10.3	656.6	36.8	22.9	32.3	81.6
M2 S6	0.1	14.0	0.1	196.3	2.6	0.0	998.6	12.1	9.8	26.0	602.5	79.4	29.8	71.1	24.1
M2 S7	0.1	11.0	0.1	110.2	1.8	0.0	805.6	7.9	6.1	9.5	657.1	49.5	25.4	40.6	16.5
M2 S8	0.1	11.0	0.1	295.8	1.6	0.0	760.9	8.9	10.7	71.2	426.6	51.3	41.9	21.2	10.7
M2 S8 Dupl	0.2	11.0	0.1	277.5	1.3	0.0	489.0	8.1	10.2	67.7	468.5	39.5	40.9	22.2	7.8
M2 S9	0.1	11.0	0.2	248.0	1.6	0.0	656.6	8.7	12.1	42.6	335.0	61.8	40.2	22.0	12.4
M2 S10	0.1	12.0	0.2	91.3	1.8	0.0	913.1	1.1	5.5	13.3	334.4	68.2	31.7	27.0	13.1
M3 S1	0.4	13.0	0.2	316.0	2.1	0.0	897.2	12.5	4.7	58.5	580.9	43.8	37.2	25.8	15.3
M3 52	0.1	13.0	0.2	72.6	1.7	0.0	878.8	16.5	4.7	9.7	374.7	54.8	20.4	26.0	12.3
M3 53	0.2	12.0	0.3	94.3	1.8	0.0	821.6	20.7	6.6	11.7	426.1	//./	22.7	26.9	31.3
M3 54 M2 S4 Dupl	1.2	12.0	0.3	80.7	1.9	0.0	877.2	24.9	4.7	17.2	1399.3	98.1	20.9	32.9	93.1
M3 54 Dupi M3 55	1.0	11.0	0.2	02.2	2.4	0.0	920.0	25.0	0.3 5 7	10.0	1457.9	105.4	28.0	35.0	107.8
M3 55 M3 56	0.4	14.0	0.4	93.2	2.2	0.0	002.9	21.5	3.7	161.2	419.4	75.0	24.2	30.2	49.0
M3 50 M3 57	0.5	12.0	0.2	00.5	2.2	0.0	030.0	10.9	7.3	101.3	410.4	30.9	47.7	43.7	19.7
M3 58	3.4	10.0	0.2	70.1	1.0	0.0	877.3	27.0	8.4	15.2	1/185 /	73.0	20.2	36.1	150.6
M3 S9	3.4	10.0	0.4	68.3	1.0	0.0	831.6	27.5	5.1	15.2	1276.1	88.2	20.2	31.7	115.0
M3 S9 Dupl	2.9	10.0	0.2	69.1	21	0.0	846.6	26.7	5.2	15.8	1432.4	91.4	22.4	40.5	134.1
M4 S1	0.3	10.0	0.4	166.9	17	0.0	938.4	16.7	44	7 9	267.7	13.1	16.0	26.5	16
M4 S1 Dupl	0.0	10.0	0.2	209.2	16	0.0	838.4	16.8	4.3	87	272.8	12.3	16.0	33.2	1.0
M4 S2	0.3	10.0	0.2	41.4	0.8	0.0	841.6	15.3	4.2	4.3	151.6	9.1	11.9	20.8	0.0
M4 S3	0.1	11.0	0.0	67.7	1.3	0.0	994.7	8.1	4.5	10.9	196.4	21.4	16.4	29.5	0.0
M4 S4	0.1	11.0	0.1	48.2	1.3	0.0	937.2	5.8	4.5	3.1	139.3	38.9	14.0	23.6	2.1
M4 S5	1.5	11.0	0.1	62.1	1.2	0.0	836.2	7.8	4.4	6.2	593.8	60.5	17.9	23.7	46.0
M4 S6	0.2	10.0	0.1	63.8	1.3	0.0	980.2	3.8	5.5	9.2	178.7	11.7	13.5	25.3	0.0
M4 S7	0.1	11.0	0.1	75.6	1.4	0.0	1163.7	4.0	6.2	6.8	117.0	20.9	11.2	23.5	0.0
M4 S8	0.2	11.0	0.1	118.7	1.6	0.0	1034.9	5.8	8.1	10.5	106.8	27.7	12.0	25.5	3.3
M4 S9	0.1	12.0	0.2	93.8	2.0	0.0	608.1	11.4	6.7	7.7	158.9	16.4	19.3	49.1	13.6
M4 S10	0.3	12.0	0.2	63.3	0.9	0.0	385.1	6.5	5.9	4.5	79.4	17.2	11.0	21.7	1.2
M4 S10 Dupl	0.4	12.0	0.1	82.3	1.8	0.0	932.7	7.6	7.6	6.0	113.0	32.0	10.8	21.8	8.6
Average	0.5	11.5	0.3	126.6	2.0	0.0	849.2	17.0	7.3	20.8	443.7	38.9	20.1	31.4	27.1

Table 10.9a. Trace elements values (ppm) of ICP-MS duplicate bauxite samples prepared using the multi-acid attack – dissolution procedure

(quality control).

Sample Name	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
M1 S7	0.5	45.6	68.8	4.7	2.4	0.0	18.2	825.2	6.5	43.9	6.3	15.5	4.5	58.8	307.4	34.5	0.9	7.9	12.4	10.9	31.3	5.0	365.7	202.5	12.2	562.1
M1 S7 ICP-Dupl	0.2	49.8	68.7	4.0	2.1	0.0	20.1	1209.5	6.7	57.7	6.5	16.1	2.9	69.7	325.6	39.6	0.0	8.0	12.2	9.5	39.1	4.6	454.5	191.3	9.7	664.0
Average	0.3	47.7	68.7	4.3	2.2	0.0	19.2	1017.4	6.6	50.8	6.4	15.8	3.7	64.3	316.5	37.1	0.5	7.9	12.3	10.2	35.2	4.8	410.1	196.9	10.9	613.1
Sample-Dupl	0.3	-4.2	0.0	0.7	0.3	0.0	-1.9	-384.3	-0.2	-13.7	-0.2	-0.6	1.6	-10.9	-18.2	-5.1	0.9	-0.1	0.2	1.4	-7.8	0.4	-88.8	11.2	2.5	-101.9
M2 S7	0.1	110.2	49.5	3.9	1.8	0.0	24.6	805.6	7.9	45.4	6.1	13.8	9.5	60.5	657.1	49.5	0.2	25.4	12.2	9.5	26.0	7.2	411.3	302.5	16.5	539.3
M2 S7 ICP-Dupl	0.2	123.5	51.0	4.9	1.9	0.0	29.7	915.0	9.2	48.0	7.4	13.7	9.4	66.9	742.9	48.2	0.2	26.1	15.5	8.8	31.3	7.8	462.9	291.0	19.2	579.9
Average	0.1	116.8	50.2	4.4	1.8	0.0	27.2	860.3	8.5	46.7	6.7	13.8	9.5	63.7	700.0	48.8	0.2	25.8	13.9	9.1	28.7	7.5	437.1	296.8	17.8	559.6
Sample-Dupl	0.0	-13.4	-1.5	-1.0	-0.1	0.0	-5.1	-109.4	-1.3	-2.6	-1.2	0.1	0.0	-6.4	-85.8	1.3	-0.1	-0.7	-3.3	0.7	-5.3	-0.6	-51.7	11.5	-2.7	-40.6
M3 S4 Dupl	0.2	81.0	49.9	9.8	2.4	0.0	130.4	926.6	25.0	57.3	6.3	18.8	18.6	89.5	1457.9	105.4	0.5	28.0	26.6	32.0	41.6	10.3	786.2	180.4	107.7	617.6
M3 S4 Dupl ICP-Dupl	0.2	79.6	49.5	12.5	1.4	0.0	109.3	915.0	26.2	50.3	5.9	14.2	16.5	64.1	1217.0	99.8	0.5	20.1	24.4	7.9	27.9	9.6	776.1	177.1	95.5	594.4
Average	0.2	80.3	49.7	11.2	1.9	0.0	119.9	920.8	25.6	53.8	6.1	16.5	17.5	76.8	1337.5	102.6	0.5	24.0	25.5	19.9	34.8	10.0	781.2	178.8	101.6	606.0
Sample-Dupl	0.0	1.4	0.4	-2.6	1.0	0.0	21.1	11.7	-1.2	7.0	0.4	4.6	2.1	25.4	240.9	5.6	0.0	7.9	2.3	24.1	13.7	0.7	10.1	3.3	12.3	23.2
M4 S10 Dupl	0.1	82.3	24.9	4.6	1.8	0.0	35.2	932.7	7.6	61.5	7.6	13.3	6.0	76.0	113.0	32.0	0.0	10.8	12.2	11.6	31.1	5.3	523.4	113.6	8.6	514.6
M4 S10 Dupl ICP-Dupl	0.1	85.7	28.4	5.5	1.9	0.0	43.2	1000.3	8.5	60.7	7.9	13.8	5.9	75.8	126.6	33.1	0.0	9.5	14.2	8.5	30.7	5.9	541.5	121.6	10.1	548.3
Average	0.1	84.0	26.7	5.0	1.8	0.0	39.2	966.5	8.1	61.1	7.8	13.6	6.0	75.9	119.8	32.6	0.0	10.1	13.2	10.1	30.9	5.6	532.4	117.6	9.4	531.5
Sample-Dupl	0.0	-3.5	-3.5	-1.0	-0.1	0.0	-8.1	-67.6	-0.9	0.8	-0.3	-0.6	0.1	0.2	-13.6	-1.1	0.0	1.3	-2.0	3.1	0.4	-0.6	-18.1	-8.0	-1.5	-33.8
M4 S2	0.2	41.4	24.4	3.3	0.8	0.0	9.4	841.6	15.3	39.5	4.2	8.6	4.3	52.3	151.6	9.1	0.0	11.9	7.0	6.6	11.9	3.5	334.9	88.7	0.0	326.4
M4 S2 ICP-Dupl	0.1	44.1	26.1	3.2	1.4	0.0	11.7	895.8	15.0	44.8	3.7	9.5	4.3	54.6	184.5	8.2	0.0	11.4	9.9	6.4	15.9	4.0	343.1	116.5	0.0	382.8
Average	0.1	42.7	25.2	3.3	1.1	0.0	10.5	868.7	15.1	42.1	3.9	9.0	4.3	53.4	168.0	8.6	0.0	11.7	8.5	6.5	13.9	3.7	339.0	102.6	0.0	354.6
Sample-Dupl	0.1	-2.7	-1.7	0.0	-0.5	0.0	-2.3	-54.2	0.3	-5.3	0.5	-0.9	0.0	-2.3	-32.9	0.9	0.0	0.5	-2.9	0.1	-3.9	-0.5	-8.2	-27.8	0.0	-56.5

Note: The variable amount of each sample's residue has clearly effect on element results. This can be observed in element variations between the duplicates, and especially for Cr, Ni, V and Zr that occur in high concentrations in bauxite.

Table 10.9b. REE values (ppm) of ICP-MS duplicate bauxite samples prepared using the multi-acid attack – dissolution procedure (quality control).

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
M1 S7	29.3	11.7	113.3	3.5	12.2	3.0	1.0	2.9	0.9	4.0	1.1	3.0	0.8	3.1	0.8	18.1
M1 S7 ICP-Dupl	36.6	6.5	104.3	2.2	8.3	2.2	0.5	2.2	0.4	3.0	0.7	2.2	0.4	2.4	0.5	13.9
Average	32.9	9.1	108.8	2.8	10.3	2.6	0.8	2.5	0.6	3.5	0.9	2.6	0.6	2.8	0.6	16.0
Sample-Dupl	-7.2	5.2	9.0	1.3	3.9	0.8	0.5	0.8	0.5	1.0	0.4	0.7	0.3	0.7	0.4	4.1
M2 S7	40.6	3.9	109.7	1.3	5.5	1.2	0.3	1.3	0.2	1.9	0.4	1.3	0.2	1.4	0.2	7.0
M2 S7 ICP-Dupl	55.8	5.9	163.5	2.1	8.0	2.0	0.5	1.9	0.3	2.6	0.6	1.8	0.3	1.8	0.3	10.5
Average	48.2	4.9	136.6	1.7	6.7	1.6	0.4	1.6	0.2	2.2	0.5	1.6	0.3	1.6	0.3	8.8
Sample-Dupl	-15.2	-2.0	-53.8	-0.7	-2.5	-0.8	-0.2	-0.6	-0.1	-0.7	-0.2	-0.4	-0.1	-0.4	-0.1	-3.6
M3 S4 Dupl	35.0	25.5	47.5	6.0	20.9	5.5	1.3	5.8	1.3	9.5	1.8	5.5	0.9	6.3	1.0	19.0
M3 S4 Dupl ICP-Dupl	39.9	17.2	27.1	4.3	14.8	3.8	1.0	4.0	0.9	6.8	1.3	3.7	0.7	4.4	0.7	12.2
Average	37.4	21.4	37.3	5.2	17.9	4.7	1.1	4.9	1.1	8.2	1.5	4.6	0.8	5.3	0.8	15.6
Sample-Dupl	-4.9	8.3	20.4	1.7	6.1	1.7	0.4	1.8	0.4	2.7	0.5	1.7	0.2	1.9	0.2	6.8
M4 S10 Dupl	21.8	2.7	174.8	0.8	3.0	0.8	0.2	1.0	0.1	1.6	0.4	1.3	0.2	1.6	0.3	7.4
M4 S10 Dupl ICP-Dupl	31.6	2.9	119.9	0.9	3.4	1.0	0.2	1.2	0.2	1.9	0.5	1.5	0.3	1.7	0.3	7.9
Average	26.7	2.8	147.4	0.8	3.2	0.9	0.2	1.1	0.2	1.7	0.4	1.4	0.3	1.6	0.3	7.7
Sample-Dupl	-9.8	-0.2	54.9	-0.1	-0.3	-0.2	0.0	-0.2	0.0	-0.2	-0.1	-0.2	0.0	-0.2	-0.1	-0.5
	-	-											-	-		
M4 S2	20.8	0.3	8.0	0.2	0.5	0.2	0.1	0.2	0.0	0.4	0.1	0.3	0.1	0.4	0.1	1.4
M4 S2 ICP-Dupl	25.3	0.6	16.7	0.3	1.1	0.3	0.1	0.4	0.0	0.8	0.2	0.5	0.1	0.7	0.1	2.5
Average	23.1	0.4	12.4	0.2	0.8	0.3	0.1	0.3	0.0	0.6	0.2	0.4	0.1	0.5	0.1	2.0
Sample-Dupl	-4.5	-0.3	-8.7	-0.1	-0.6	-0.1	0.0	-0.2	0.0	-0.4	-0.1	-0.2	0.0	-0.2	0.0	-1.1

Note: The variable amount of each sample's residue has effect on element results. This can be observed in element variations between the duplicates, and especially for Ce. However, the ree concentrations seem to be very low, hence most of the ree's were possibly trapped in the residue.

Table 10.10a. Trace elements values (ppm) of ICP-MS of bauxite blanks prepared using the multi-acid attack – dissolution procedure (quality control).

Sample Name	Ag	As	Ва	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
Blank 1	0.00	0.01	0.02	0.00	0.00	< 0.00	< 0.00	0.01	0.01	0.00	0.00	0.02	0.01	0.05	0.01	< 0.00	0.00	0.03	0.01	0.02	0.02	0.00	0.01	0.60	<0.00	0.63
Blank 2	0.00	0.00	0.02	0.00	0.00	< 0.00	<0.00	0.01	0.02	0.00	0.00	0.02	0.01	0.02	0.01	< 0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.62	<0.00	0.64
Blank 3	0.00	0.00	0.00	0.00	< 0.00	< 0.00	< 0.00	0.01	0.01	0.00	0.00	< 0.00	0.00	0.01	<0.00	< 0.00	<0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.04	<0.00	0.02
Blank 4	0.00	0.00	0.00	0.00	< 0.00	< 0.00	< 0.00	0.01	0.01	0.00	0.00	< 0.00	0.00	0.01	<0.00	< 0.00	<0.00	0.00	0.00	0.00	< 0.00	0.00	0.01	0.04	<0.00	0.02
Blank 5	0.00	0.00	0.03	0.00	< 0.00	< 0.00	< 0.00	0.01	0.01	0.01	0.00	< 0.00	0.00	0.01	0.01	<0.00	0.00	0.00	0.11	< 0.00	0.00	0.00	0.03	0.02	<0.00	0.02
Blank 6	0.00	0.00	0.05	0.00	0.00	< 0.00	< 0.00	0.01	0.01	0.01	0.00	< 0.00	0.00	0.00	0.10	< 0.00	0.00	0.00	0.07	< 0.00	0.00	0.00	0.03	0.02	<0.00	0.02

Table 9.10b. REE values (ppm) of ICP-MS of bauxite blanks prepared using the multi-acid attack – dissolution procedure (quality control).

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
Blank 1	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	<0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Blank 2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	<0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Blank 3	0.00	0.00	0.00	0.00	0.00	< 0.00	0.00	0.00	<0.00	0.00	0.00	0.00	0.00	0.00	0.00	< 0.00
Blank 4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	<0.00	0.00	0.00	0.00	0.00	0.00	0.00	< 0.00
Blank 5	0.01	0.04	0.05	0.01	0.02	0.00	0.00	0.00	< 0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Blank 6	0.01	0.03	0.03	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01

Note: ICP-MS blanks gave almost zero results. Hence, there was no sample contamination during the whole process.

Table 10.11a. Trace element values (ppm) of ICP-MS duplicate bauxite samples prepared using the lithium borate fusion – dissolution procedure (quality control).

Sample Name	Ва	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	V	W	Zr
M4 S2	41	4	25.1	0.3	60.6	12.2	45.1	0.9	10	26.4	3.9	41.4	5.8	420	84.7	442.8
M4 S2 ICP-Dupl	42	7	26.4	0.3	63.8	12.7	45.6	0.6	11	27.5	3.9	42.2	6	419	83.6	443.4
Average	41.5	5.5	25.8	0.3	62.2	12.5	45.4	0.8	10.5	27.0	3.9	41.8	5.9	419.5	84.2	443.1
Sample-Dupl	-1.0	-3.0	-1.3	0.0	-3.2	-0.5	-0.5	0.3	-1.0	-1.1	0.0	-0.8	-0.2	1.0	1.1	-0.6

Table 10.11b. REE values (ppm) of ICP-MS duplicate bauxite samples prepared using the lithium borate fusion – dissolution procedure (quality control).

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
M4 S2	9.0	162.0	2.4	9.8	2.3	0.5	3.2	0.7	4.6	1.0	3.2	0.5	3.6	0.6	29.0
M4 S2 ICP-Dupl	8.4	161.9	2.4	9.6	2.4	0.6	3.3	0.6	4.9	1.0	3.2	0.5	3.6	0.6	29.4
Average	8.7	162.0	2.4	9.7	2.3	0.6	3.3	0.6	4.8	1.0	3.2	0.5	3.6	0.6	29.2
Sample-Dupl	0.6	0.1	0.0	0.2	-0.1	-0.1	-0.1	0.0	-0.3	0.0	0.0	0.0	-0.1	0.0	-0.4

Note: Variations of ICP-MS duplicates appear to be extremely low.

Table 10.12a. Trace element values (ppm) of ICP-MS of blanks prepared using the lithium borate fusion – dissolution procedure (quality control)

Sample Name	Ba	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	V	W	Zr
Blank 1	<1	<1	<0.2	<0.1	<0.5	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	<0.1
Blank 2	<1	<1	<0.2	0.2	<0.5	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	0.4

Table 10.12b. REE values (ppm) of ICP-MS of blanks prepared using the lithium borate fusion – dissolution procedure (quality control)

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
Blank 1	<0.1	<0.1	< 0.02	<0.3	< 0.05	< 0.02	< 0.05	<0.01	< 0.05	< 0.02	< 0.03	<0.01	< 0.05	<0.01	<0.1
Blank 2	<0.1	<0.1	<0.02	<0.3	< 0.05	<0.02	< 0.05	<0.01	< 0.05	<0.02	< 0.03	<0.01	<0.05	<0.01	<0.1

Note: ICP-MS blanks gave almost zero results. Hence, there was no sample contamination during the whole process.

Table 10.13a. Trace element recovery values (ppm) of red mud waste samples prepared using the lithium borate fusion – dissolution procedure in comparison with 4 acids attack.

Sample Name	Ba (ACM E)	Ba (CSM )	Dissolve d %	Be (ACM E)	Be (CSM )	Dissolve d %	Co (ACM E)	Co (CSM )	Dissolve d %	Ga (ACM E)	Ga (CSM )	Dissolve d %	Hf (ACM E)	Hf (CSM )	Dissolve d %	Nb (ACM E)	Nb (CSM )	Dissolve d %	Rb (ACM E)	Rb (CSM )	Dissolve d %
SqA S4	94.0	98.7	105.0	4.0	6.0	149.3	48.2	55.5	115.1	45.2	72.8	161.0	28.3	26.4	93.3	86.4	108.2	125.2	5.9	4.9	83.6
SqB S4	91.0	95.2	104.6	6.0	5.7	95.6	49.1	46.8	95.3	50.2	70.3	139.9	26.9	24.8	92.0	80.2	97.9	122.1	5.5	1.9	34.4
SqZ S C2	79.0	96.8	122.5	6.0	5.5	92.2	53.3	62.7	117.5	40.5	69.8	172.4	30.6	24.8	81.0	95.4	120.4	126.2	4.2	3.9	93.7
Average	88.0	96.9	110.7	5.3	5.7	112.4	50.2	55.0	109.3	45.3	71.0	157.8	28.6	25.3	88.8	87.3	108.8	124.5	5.2	3.6	70.5

Table 10.13b. Trace element recovery values (ppm) of red mud waste samples prepared using the lithium borate fusion – dissolution procedure in comparison with 4 acids attack.

Comple Nome	Sr	Sr	Dissolved	Та	Та	Dissolved	Th	Th	Dissolved	U	U	Dissolved	V	V	Dissolved	w	W	Dissolved	Zr	Zr	Dissolved
Sample Name	(ACME)	(CSM)	%																		
SqA S4	145.1	149.3	102.9	6.7	17.4	259.2	86.9	79.6	91.6	10.8	11.2	103.5	852.0	832.1	97.7	26.2	40.1	153.2	1001.9	925.4	92.4
SqB S4	109.0	95.6	87.7	6.0	13.1	217.6	83.3	69.2	83.1	12.7	10.4	81.9	947.0	890.6	94.0	42.9	45.4	105.7	942.5	881.0	93.5
SqZ S C2	113.2	125.9	111.2	7.2	12.3	171.4	95.6	92.2	96.4	13.5	12.9	95.4	974.0	983.4	101.0	21.4	24.9	116.5	1089.5	915.9	84.1
Average	122.4	123.6	100.6	6.6	14.3	216.1	88.6	80.3	90.4	12.3	11.5	93.6	924.3	902.0	97.6	30.2	36.8	125.1	1011.3	907.4	90.0

Note: All element recoveries are around ±100% apart from Ga, Rb and Ta. This is more likely due to partial dissolutions or to potential element variations in the same sample. The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results represent the total amount of each element in the sample.

Table 10.13c. REE recovery values (ppm) of red mud waste samples prepared using the lithium borate fusion – dissolution procedure in comparison with 4 acids attack.

Sample	La	La	Dissolv	Ce	Ce	Dissolv	Pr	Pr	Dissolv	Nd	Nd	Dissolv	Sm	Sm	Dissolv	Eu	Eu	Dissolv	Gd	Gd	Dissolv	Tb	Tb	Dissolve
Name	(ACME)	(CSM)	ed %	(ACME)	(CSM)	d %																		
SqA S4	134.9	134.3	99.5	416.9	421.1	101.0	29.5	30.5	103.4	107.4	112.3	104.6	20.5	21.2	103.1	4.6	4.6	101.7	19.3	17.5	90.6	3.1	3.3	103.6
SqB S4	117.2	81.5	69.6	391.3	336.0	85.9	27.0	21.9	81.3	99.0	82.7	83.5	19.1	17.2	90.3	4.3	3.9	90.8	17.8	14.3	80.4	2.9	2.7	94.9
SqZ S C2	129.3	141.5	109.4	421.0	463.2	110.0	28.3	33.4	118.1	104.0	123.4	118.7	20.5	24.3	118.3	4.4	5.1	116.4	19.6	20.2	103.3	3.0	3.4	112.8
Average	127.1	119.1	92.8	409.7	406.8	99.0	28.3	28.6	100.9	103.5	106.1	102.2	20.0	20.9	103.9	4.4	4.6	103.0	18.9	17.3	91.4	3.0	3.1	103.8

Table 10.13d. REE red mud waste values (ppm) of bauxite samples prepared using the lithium borate fusion – dissolution procedure in comparison with 4 acids attack.

Sample Name	Dy (ACME)	Dy (CSM)	Dissolved %	Ho (ACME)	Ho (CSM)	Dissolved %	Er (ACME)	Er (CSM)	Dissolved %	Tm (ACME)	Tm (CSM)	Dissolved %	Yb (ACME)	Yb (CSM)	Dissolved %	Lu (ACME)	Lu (CSM)	Dissolved %	Y (ACME)	Y (CSM)	Dissolved %
SqA S4	19.8	18.0	91.0	4.1	3.8	94.4	12.5	11.2	89.9	2.0	2.0	98.9	13.4	12.4	92.9	2.1	2.1	102.4	106.2	84.3	79.4
SqB S4	18.3	14.9	81.4	3.7	3.3	89.7	11.0	9.3	84.2	1.8	1.8	100.3	12.3	10.3	84.3	1.9	1.9	104.0	95.4	64.8	67.9
SqZ S C2	19.9	21.1	106.2	4.0	4.2	105.2	11.9	12.4	104.5	2.0	2.0	100.7	13.5	13.6	101.0	2.1	2.1	99.6	95.2	96.5	101.4
Average	19.3	18.0	92.9	3.9	3.8	96.5	11.8	11.0	92.9	1.9	1.9	99.9	13.0	12.1	92.7	2.0	2.0	102.0	98.9	81.9	82.9

Note: All ree recoveries are impressively around ±100%, excluding SqB S4 sample that shows partial dissolution, with all ree's being slightly lower compared to the fusion results. The 4 acid attack dissolution percentage was estimated by (CSM element value/ACME element value)%, assuming that ACME results represent the total amount of each element in the sample.

Table 10.13e. Rest of trace elements values (ppm) of red mud waste samples prepared using lithium borate fusions or the 4 acids attack.

Sample Name	Cs (ACME)	Sn (ACME)	Ag (CSM)	As (CSM)	Bi (CSM)	Cd (CSM)	Cr (CSM)	Cu (CSM)	Ge (CSM)	Mo (CSM)	Ni (CSM)	Pb (CSM)	Sb (CSM)	Sc (CSM)	Zn (CSM)
SqA S4	1.3	19.0	0.6	231.2	5.3	0.9	1695.3	48.3	20.4	35.9	765.9	130.7	27.5	99.0	69.1
SqB S4	1.2	18.0	0.6	237.3	4.4	0.9	1680.9	42.2	16.9	38.1	857.8	110.8	29.0	82.2	51.2
SqZ S C2	1.7	21.0	0.2	199.0	4.9	0.4	1782.5	45.4	21.0	16.7	997.3	139.2	31.2	120.8	55.1
Average	1.4	19.3	0.5	222.5	4.9	0.7	1719.6	45.3	19.4	30.2	873.7	126.9	29.2	100.7	58.4

Table 10.14a. Trace elements values (ppm) of ICP-MS duplicate red mud waste samples prepared using the lithium borate fusion – dissolution procedure (quality control).

Sample Name	Ва	Be	Со	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Та	Th	U	V	W	Zr
SqB S4	91.0	6.0	49.1	1.2	50.2	26.9	80.2	5.5	18.0	109.0	6.0	83.3	12.7	947.0	42.9	942.5
SqB S4 ICP-Dupl	98.0	3.0	46.2	1.2	48.2	27.0	83.0	5.4	18.0	110.2	6.7	83.3	12.5	922.0	43.4	940.4
Average	94.5	4.5	47.7	1.2	49.2	27.0	81.6	5.5	18.0	109.6	6.4	83.3	12.6	934.5	43.2	941.5
Sample-Dupl	-7.0	3.0	2.9	0.0	2.0	-0.1	-2.8	0.1	0.0	-1.2	-0.7	0.0	0.2	25.0	-0.5	2.1

Table 10.14b. REE values (ppm) of ICP-MS duplicate red mud waste samples prepared using the lithium borate fusion – dissolution procedure (quality control).

Sample Name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
SqB S4	117.2	391.3	27.0	99.0	19.1	4.3	17.8	2.9	18.3	3.7	11.0	1.8	12.3	1.9	95.4
SqB S4 ICP-Dupl	118.4	400.5	27.2	101.6	19.6	4.3	18.0	2.9	19.0	3.7	11.3	1.8	12.0	1.9	90.9
Average	117.8	395.9	27.1	100.3	19.3	4.3	17.9	2.9	18.7	3.7	11.1	1.8	12.1	1.9	93.2
Sample-Dupl	-1.2	-9.2	-0.1	-2.6	-0.5	0.0	-0.2	0.0	-0.7	0.0	-0.2	0.0	0.3	0.0	4.5

Note: Variations of ICP-MS duplicates appear to be extremely low.

Note: Red mud waste and bauxite fused samples were analyzed on the same run. Therefore the blank samples used are the same. For results see Table 10.12 (a and b) above.

Sample Name	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	w	Zn	Zr
SqA S1	0.6	232.8	85.8	5.6	6.9	0.8	47.6	1610.9	53.0	65.0	18.2	31.2	42.5	125.6	685.4	113.7	3.0	39.5	133.6	33.4	88.2	8.8	868.4	65.8	68.1	892.1
SqA S2	0.5	238.8	92.3	5.7	5.4	0.7	51.4	1746.4	58.0	67.6	19.3	27.5	35.3	114.8	726.8	120.0	2.3	29.5	147.4	22.9	77.8	9.2	920.6	49.2	71.2	939.2
SqA S3	0.6	211.6	91.1	7.4	5.0	0.9	49.3	1563.9	51.0	68.7	19.0	24.2	28.3	100.6	661.1	116.0	4.0	24.4	137.5	17.5	72.5	10.4	752.2	33.6	63.9	850.8
SqA S4	0.6	231.2	98.7	6.0	5.3	0.9	55.5	1695.3	48.3	72.8	20.4	26.4	35.9	108.2	765.9	130.7	4.9	27.5	149.3	17.4	79.6	11.2	832.1	40.1	69.1	925.4
SqB S1	0.6	234.1	89.6	8.2	4.6	1.0	48.0	1723.2	44.6	63.5	18.6	24.9	24.4	101.4	925.8	119.0	1.3	29.0	106.5	14.8	65.8	8.9	978.0	43.3	52.9	883.1
SqB S2	0.6	234.1	94.8	6.3	4.8	0.9	51.2	1794.7	44.5	71.8	19.9	25.8	21.5	103.5	950.3	125.3	1.8	28.5	114.5	14.5	78.1	10.7	1025.0	43.0	58.1	926.3
SqB S3	0.6	246.6	97.8	10.5	4.9	0.8	53.6	1707.4	45.6	71.7	18.6	24.5	22.5	98.3	941.6	126.1	2.9	29.4	116.3	13.6	78.1	11.7	963.9	43.7	61.5	878.5
SqB S4	0.6	237.3	95.2	5.7	4.4	0.9	46.8	1680.9	42.2	70.3	16.9	24.8	38.1	97.9	857.8	110.8	1.9	29.0	95.6	13.1	69.2	10.4	890.6	45.4	51.2	881.0
SqZ S A1	0.6	215.9	80.6	6.7	4.5	0.6	60.5	1440.4	39.2	62.0	18.4	22.3	17.4	103.6	1002.6	127.2	3.1	28.0	110.5	12.8	78.4	10.9	1028.6	34.3	47.3	791.5
SqZ S A2	0.6	218.5	83.2	6.0	4.7	0.8	61.7	1418.8	38.2	62.4	19.6	21.9	16.4	102.8	1006.9	129.6	3.4	27.7	113.0	12.0	79.6	11.3	1032.2	34.3	43.3	793.2
SqZ S A3	0.4	223.3	80.9	6.2	5.1	0.5	62.3	1535.3	32.4	65.0	19.1	25.0	18.8	127.2	1031.2	128.4	2.1	36.3	116.0	17.0	83.7	10.8	1009.1	43.7	34.0	814.7
SqZ S B1	0.3	191.8	89.5	5.2	5.0	0.5	68.2	1687.5	46.1	66.8	20.3	25.6	16.9	123.2	1107.6	132.7	3.1	32.1	111.3	13.7	88.9	12.3	932.5	29.6	61.0	923.2
SqZ S B2	0.3	190.5	94.1	8.8	4.9	0.3	69.1	1685.3	44.9	67.7	21.3	25.8	16.8	119.9	1120.3	135.0	4.6	30.9	115.3	13.3	92.5	12.6	982.4	27.0	63.8	932.9
SqZ S B3	0.3	192.3	94.5	5.3	4.7	0.5	68.6	1690.2	44.6	68.0	19.9	25.2	16.3	118.4	1101.5	132.2	4.2	30.3	112.2	12.4	92.8	12.5	964.4	26.0	58.9	924.0
SqZ S C1	0.3	193.2	89.0	5.4	4.5	0.3	56.8	1619.6	39.3	62.1	19.1	23.1	15.4	112.7	938.2	127.2	2.3	30.2	116.4	11.6	83.8	11.6	936.4	21.8	45.4	855.4
SqZ S C2	0.2	199.0	96.8	5.5	4.9	0.4	62.7	1782.5	45.4	69.8	21.0	24.8	16.7	120.4	997.3	139.2	3.9	31.2	125.9	12.3	92.2	12.9	983.4	24.9	55.1	915.9
SqZ S C3	0.2	195.1	91.4	6.1	4.7	0.6	61.6	1768.1	41.0	69.8	20.5	24.5	16.0	116.8	979.2	135.6	3.0	31.5	121.3	11.7	89.7	12.4	960.2	23.1	48.3	910.5
SqZ S C4	0.2	193.1	89.8	5.6	4.6	0.4	60.0	1710.4	41.2	65.1	20.3	23.5	15.8	113.4	950.4	133.2	3.2	30.7	115.2	11.2	87.2	12.2	980.2	22.2	50.4	878.5
Average	0.5	215.5	90.8	6.5	4.9	0.7	57.5	1658.9	44.4	67.2	19.5	25.0	23.0	111.6	930.6	126.8	3.1	30.3	119.9	15.3	82.1	11.2	946.7	36.2	55.7	884.2

Table 10.15a. Trace elements values (ppm) of all red mud waste samples prepared using the multi-acid attack – dissolution procedure.

Table 10.15b. REE values (ppm) of all red mud waste samples prepared using the multi-acid attack – dissolution procedure.

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
SqA S1	91.7	109.9	347.7	25.8	95.1	18.2	4.0	14.9	2.7	15.6	3.4	9.9	1.7	11.0	1.8	74.1
SqA S2	100.0	122.0	380.7	29.3	107.1	21.1	4.5	16.9	3.1	17.8	3.7	11.2	1.9	12.6	2.0	83.3
SqA S3	90.7	126.1	386.3	29.4	107.5	20.9	4.6	16.7	3.2	16.8	3.7	10.4	1.9	11.5	2.0	79.3
SqA S4	99.0	134.3	421.1	30.5	112.3	21.2	4.6	17.5	3.3	18.0	3.8	11.2	2.0	12.4	2.1	84.3
SqB S1	87.0	89.7	312.1	23.2	87.4	17.5	4.0	14.6	2.8	15.6	3.3	9.8	1.8	11.0	2.0	68.8
SqB S2	100.6	107.7	383.1	27.1	102.2	20.3	4.5	17.1	3.2	17.5	3.8	11.3	2.0	12.3	2.1	81.2
SqB S3	99.4	122.2	405.7	29.5	110.6	21.3	4.7	17.6	3.3	18.0	3.8	11.0	1.9	12.1	2.1	83.5
SqB S4	82.2	81.5	336.0	21.9	82.7	17.2	3.9	14.3	2.7	14.9	3.3	9.3	1.8	10.3	1.9	64.8
SqZ S A1	100.5	130.3	367.1	30.1	112.8	22.6	4.9	19.4	3.5	20.0	4.1	11.9	2.1	12.7	2.2	89.9
SqZ S A2	98.5	138.6	373.9	32.1	120.6	24.0	5.2	20.5	3.7	20.2	4.2	12.0	2.1	13.1	2.2	90.3
SqZ S A3	99.9	126.9	369.5	29.7	111.9	22.0	4.7	18.6	3.3	19.1	3.9	11.3	1.9	12.0	1.9	83.3
SqZ S B1	103.3	123.5	411.7	28.9	106.8	21.7	4.4	18.2	3.0	18.4	3.6	11.1	1.7	12.0	1.7	87.3
SqZ S B2	108.8	127.1	433.2	30.0	111.9	22.7	4.8	19.6	3.2	20.1	3.9	11.8	1.9	12.8	1.9	95.3
SqZ S B3	111.0	126.8	437.0	29.8	114.1	22.8	4.7	19.5	3.3	20.2	3.9	11.9	1.8	13.1	1.9	96.7
SqZ S C1	112.1	123.0	398.0	29.1	105.6	21.5	4.4	17.8	3.0	19.5	3.8	11.5	1.8	12.8	1.9	87.7
SqZ S C2	120.8	141.5	463.2	33.4	123.4	24.3	5.1	20.2	3.4	21.1	4.2	12.4	2.0	13.6	2.1	96.5
SqZ S C3	120.4	138.0	444.1	32.1	117.8	23.6	4.9	19.4	3.3	20.5	4.1	12.4	1.9	13.6	2.0	93.7
SqZ S C4	112.0	130.3	438.0	30.2	112.6	22.4	4.6	18.8	3.2	19.8	4.0	11.9	1.9	13.1	2.0	91.7
Average	102.1	122.2	394.9	29.0	107.9	21.4	4.6	17.9	3.2	18.5	3.8	11.2	1.9	12.3	2.0	85.1
Table 10.16a. Trace elements values (ppm) of ICP-MS red mud waste blanks prepared using the multi-acid attack – dissolution procedure (quality control).

Sample Name	Ag	As	Ва	Be	Bi	Cd	Со	Cr	Cu	Ga	Ge	Hf	Мо	Nb	Ni	Pb	Rb	Sb	Sr	Та	Th	U	V	W	Zn	Zr
Blank 1	0.00	0.01	0.00	<0.00	0.00	0.00	<0.00	0.01	0.00	<0.00	0.00	<0.00	0.00	0.00	0.00	0.01	<0.00	0.00	0.01	<0.00	0.00	0.00	0.00	< 0.00	<0.00	0.02
Blank 2	0.00	0.00	0.02	< 0.00	0.00	0.00	<0.00	0.01	0.00	0.00	0.00	<0.00	0.00	0.00	0.01	0.01	0.00	<0.00	0.04	<0.00	0.00	0.00	0.01	< 0.00	<0.00	0.02

Note: ICP-MS blanks gave almost zero results. Hence, there was no sample contamination during the whole process.

Table 10.16b. REE values (ppm) of ICP-MS of red mud waste blanks prepared using the multi-acid attack – dissolution procedure (quality control).

Sample Name	Sc	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
Blank 1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	< 0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Blank 2	0.00	0.01	0.02	0.00	0.01	0.00	0.00	0.00	< 0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note: ICP-MS blanks gave almost zero results. Hence, there was no sample contamination during the whole process.

Appendix E: Electron Microscopy Analysis Supplementary



Figure 10.27. BSE image of zircon crystal (Zr) in a hematite (Ht) pisolith (left) in sample M2 S6 and its EDS spectrum (right).



Figure 10.28. BSE image of zircon crystal containing small amounts of Sc and its EDS spectrum, near hematite crystals in bauxite's matrix in sample M1 S1.



Figure 10.29. BSE image of barite crystal in sample M4 S4 and its EDS spectrum.



Figure 10.30. BSE image of detrital chromite crystal in sample M4 S4 and its EDS spectrum.



Figure 10.31. BSE image of detrital chromite crystal in sample M1 S1 and its EDS spectrum.



Figure 10.32. BSE image of AI, Si and Fe intermixed crystals in sample M4 S6 and their EDS spectrum.



Figure 10.33. BSE image of copper crystal in sample M4 S4 and its EDS spectrum. It is likely to be part of the copper tape used on the polished blocks for the SEM analysis and stuck on the sample rather than be included in bauxite.



Figure 10.34. BSE image of anatase crystal in a broken Al pisolith and its EDS spectrum. Near it also occurs a hematite crystal again in an Al pisolith. Sample M4 S6.



Figure 10.35. BSE image of a Ce oxide crystal containing small amounts of Ca and its EDS spectrum in sample M1 S6.



Figure 10.36. BSE images of a high Ce, Ca and maybe Eu and P bearing oxide and its EDS spectrum in sample M2 S6. REE minerals occur in Al matrix that also contains hematite (Ht) grains. The Al peak on the spectrum is due to the Al matrix near the REE crystals. Zircon (Zr) detrital crystals are also present and appear similar to the REE crystals. However, zircon crystals are euhedral and edgy compared to the REE ones, revealing that were transferred from the parent rock.

Table 10.17a. SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 1 Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anai. No.	1						2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI					Al <sub>2</sub> O <sub>3</sub>		AI	2.66	0.44	4.92	5.02	Al <sub>2</sub> O <sub>3</sub>	2.7
Si					SiO <sub>2</sub>		Si	1.26	0.36	2.24	2.69	SiO <sub>2</sub>	1.23
Ca	3.41	0.34	5.1	4.77	CaO	2.8	Ca	2.8	0.31	3.48	3.91	CaO	1.91
Fe	3.98	0.61	4.28	5.12	FeO	2.35	Fe	9.33	0.69	8.33	12	FeO	4.58
Ce	72.65	1.31	31.13	85.09	Ce <sub>2</sub> O <sub>3</sub>	17.07	Ce	62.18	1.31	22.14	72.83	Ce <sub>2</sub> O <sub>3</sub>	12.17
Th	4.41	1.07	1.14	5.02	ThO <sub>2</sub>	0.63	Th	3.11	1.04	0.67	3.54	ThO <sub>2</sub>	0.37
0	15.55	0.91	58.35			32	0	18.67	0.99	58.22			32
Totals	100						Totals	100					
					Cation Sum	22.84						Cation Sum	22.97
Anal. No.	3						4						
Anal. No. Element	3 Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	4 Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
Anal. No. Element	3 Weight % 3.47	Weight % Sigma	Atomic % 6.19	Compound % 6.56	Formula Al <sub>2</sub> O <sub>3</sub>	Number of lons 3.41	4 Element Al	Weight % 4.83	Weight % Sigma	Atomic % 8.47	Compound % 9.12	Formula	Number of lons 4.63
Anal. No. Element Al Si	3 Weight % 3.47 1.28	Weight % Sigma 0.48 0.39	Atomic % 6.19 2.19	Compound % 6.56 2.74	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	Number of lons 3.41 1.21	4 Element Al Si	Weight % 4.83 1.21	Weight % Sigma 0.51 0.36	Atomic % 8.47 2.03	Compound % 9.12 2.58	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	Number of lons 4.63 1.11
Anal. No. Element Al Si Ca	3 Weight % 3.47 1.28 2.72	Weight % Sigma 0.48 0.39 0.31	Atomic % 6.19 2.19 3.26	Compound % 6.56 2.74 3.8	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> CaO	Number of lons 3.41 1.21 1.8	4 Element Al Si Ca	Weight % 4.83 1.21 2.72	Weight % Sigma 0.51 0.36 0.31	Atomic % 8.47 2.03 3.22	Compound % 9.12 2.58 3.81	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> CaO	Number of lons 4.63 1.11 1.76
Anal. No. Element Al Si Ca Fe	3 Weight % 3.47 1.28 2.72 11.03	Weight % Sigma 0.48 0.39 0.31 0.72	Atomic % 6.19 2.19 3.26 9.5	Compound % 6.56 2.74 3.8 14.19	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> CaO FeO	Number of lons 3.41 1.21 1.8 5.24	4 Element Al Si Ca Fe	Weight % 4.83 1.21 2.72 7.49	Weight % Sigma 0.51 0.36 0.31 0.65	Atomic % 8.47 2.03 3.22 6.35	Compound % 9.12 2.58 3.81 9.63	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> CaO FeO	Number of lons 4.63 1.11 1.76 3.47
Anal. No. Element Al Si Ca Fe Ce	3 Weight % 3.47 1.28 2.72 11.03 58.29	Weight % Sigma 0.48 0.39 0.31 0.72 1.28	Atomic % 6.19 2.19 3.26 9.5 20	Compound % 6.56 2.74 3.8 14.19 68.27	Formula $A1_2O_3$ $SiO_2$ CaO FeO $Ce_2O_3$	Number of lons 3.41 1.21 1.8 5.24 11.03	4 Element Al Si Ca Fe Ce	Weight % 4.83 1.21 2.72 7.49 62.04	Weight % Sigma 0.51 0.36 0.31 0.65 1.3	Atomic % 8.47 2.03 3.22 6.35 20.96	Compound % 9.12 2.58 3.81 9.63 72.67	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> CaO FeO Ce <sub>2</sub> O <sub>3</sub>	Number of lons 4.63 1.11 1.76 3.47 11.45
Anal. No. Element Al Si Ca Fe Ce Th	3 Weight % 3.47 1.28 2.72 11.03 58.29 3.9	Weight % Sigma 0.48 0.39 0.31 0.72 1.28 0.97	Atomic % 6.19 2.19 3.26 9.5 20 0.81	Compound % 6.56 2.74 3.8 14.19 68.27 4.44	Formula $Al_2O_3$ $SiO_2$ CaO FeO $Ce_2O_3$ ThO <sub>2</sub>	Number of lons 3.41 1.21 1.8 5.24 11.03 0.45	4 Element Al Si Ca Fe Ce Th	Weight % 4.83 1.21 2.72 7.49 62.04 1.91	Weight % Sigma 0.51 0.36 0.31 0.65 1.3 0.99	Atomic % 8.47 2.03 3.22 6.35 20.96 0.39	Compound % 9.12 2.58 3.81 9.63 72.67 2.18	Formula $AI_2O_3$ $SiO_2$ CaO FeO $Ce_2O_3$ ThO <sub>2</sub>	Number of lons 4.63 1.11 1.76 3.47 11.45 0.21
Anal. No. Element Al Si Ca Fe Ce Th O	3 Weight % 3.47 1.28 2.72 11.03 58.29 3.9 19.31	Weight % Sigma 0.48 0.39 0.31 0.72 1.28 0.97 1	Atomic % 6.19 2.19 3.26 9.5 20 0.81 58.05	Compound % 6.56 2.74 3.8 14.19 68.27 4.44	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 3.41 1.21 1.8 5.24 11.03 0.45 32	4 Element Al Si Ca Fe Ce Th O	Weight % 4.83 1.21 2.72 7.49 62.04 1.91 19.79	Weight % Sigma 0.51 0.36 0.31 0.65 1.3 0.99 1	Atomic % 8.47 2.03 3.22 6.35 20.96 0.39 58.57	Compound % 9.12 2.58 3.81 9.63 72.67 2.18	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 4.63 1.11 1.76 3.47 11.45 0.21 32
Anal. No. Element Al Si Ca Fe Ce Th O Totals	3 Weight % 3.47 1.28 2.72 11.03 58.29 3.9 19.31 100	Weight % Sigma           0.48           0.39           0.31           0.72           1.28           0.97	Atomic % 6.19 2.19 3.26 9.5 20 0.81 58.05	Compound % 6.56 2.74 3.8 14.19 68.27 4.44	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 3.41 1.21 1.8 5.24 11.03 0.45 32	4 Element Al Si Ca Fe Ce Th O Totals	Weight % 4.83 1.21 2.72 7.49 62.04 1.91 19.79 100	Weight % Sigma           0.51           0.36           0.31           0.65           1.3           0.99	Atomic % 8.47 2.03 3.22 6.35 20.96 0.39 58.57	Compound % 9.12 2.58 3.81 9.63 72.67 2.18	Formula $Al_2O_3$ $SiO_2$ CaO FeO $Ce_2O_3$ ThO <sub>2</sub>	Number of lons 4.63 1.11 1.76 3.47 11.45 0.21 32

Table 10.17b. SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 2). Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anal. No.	1						2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	3.9	0.49	7.43	7.37	Al <sub>2</sub> O <sub>3</sub>	4.08	AI	3.72	0.5	7.33	7.03	Al <sub>2</sub> O <sub>3</sub>	3.99
Ca	3.22	0.31	4.13	4.51	CaO	2.27	Ca	3.33	0.32	4.41	4.66	CaO	2.4
Ti					TiO <sub>2</sub>		Ti					TiO <sub>2</sub>	
Fe	5.42	0.59	4.99	6.97	FeO	2.74	Fe	2.55	0.53	2.43	3.28	FeO	1.32
Ce	68.02	1.25	24.94	79.67		13.7	Ce	69.29	1.26	26.27	81.16		14.3
Th	1.3	0.97	0.29	1.47	ThO <sub>2</sub>	0.16	Th	3.4	0.95	0.78	3.86	ThO <sub>2</sub>	0.42
0	18.14	0.92	58.23			32	0	17.71	0.93	58.79			32
Totals	100						Totals	100					
					Cation Sum	22.95						Cation Sum	22.43
Anal. No.	3												
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons							
AI	4.34	0.5	7.66	8.19	Al <sub>2</sub> O <sub>3</sub>	4.18							
Ca	3.56	0.32	4.24	4.98	CaO	2.31							
Ti	2.71	0.4	2.7	4.53	TiO <sub>2</sub>	1.47							
Fe	6.72	0.65	5.74	8.65	FeO	3.13							
Ce	59.61	1.3	20.29	69.82	Ce <sub>2</sub> O <sub>3</sub>	11.06							
Th	3.37	1	0.69	3.83	ThO <sub>2</sub>	0.38							
0	19.69	1	58.68			32							
Totals	100												
					Cation Sum	22.53							

Table 10.17c. SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 3). Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anal. No.	1						2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	5.37	0.51	9.11	10.15	Al <sub>2</sub> O <sub>3</sub>	4.87	AI	6.83	0.57	11.67	12.9	Al <sub>2</sub> O <sub>3</sub>	6.43
Si	1.28	0.32	2.08	2.73	SiO <sub>2</sub>	1.11	Si					SiO <sub>2</sub>	
Ρ	0.37	0.33	0.54	0.84	P <sub>2</sub> O <sub>5</sub>	0.29	Р					P <sub>2</sub> O <sub>5</sub>	
Ca	2.41	0.29	2.76	3.38	CaO	1.47	Ca	2.9	0.3	3.34	4.06	CaO	1.84
Ti	1.91	0.36	1.83	3.19	TiO <sub>2</sub>	0.98	Ti					TiO <sub>2</sub>	
Fe	3.61	0.54	2.96	4.64	FeO	1.58	Fe	8.11	0.68	6.7	10.44	FeO	3.69
Ce	63.3	1.29	20.68	74.14	Ce <sub>2</sub> O <sub>3</sub>	11.05	Ce	60.57	1.25	19.95	70.94	Ce <sub>2</sub> O <sub>3</sub>	11
Th	0.82	0.88	0.16	0.93	ThO₂	0.09	Th	1.46	0.92	0.29	1.67	ThO₂	0.16
0	20.93	1.02	59.89			32	0	20.13	0.96	58.05			32
Totals	100						Totals	100					
					Cation Sum	21.43						Cation Sum	23.12

Table 10.17d SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 4). Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anal. No.							2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	7.42	0.58	12.51	14.01	Al <sub>2</sub> O <sub>3</sub>	6.74	AI	5.25	0.48	8.94	9.92	Al <sub>2</sub> O <sub>3</sub>	4.81
Si	1.12	0.35	1.82	2.41	SiO <sub>2</sub>	0.98	Si					SiO <sub>2</sub>	
Р					P <sub>2</sub> O <sub>5</sub>		Р	1.13	0.31	1.68	2.6	P₂O₅	0.91
Ca	2.77	0.3	3.15	3.88	CaO	1.7	Ca	2.36	0.29	2.7	3.3	CaO	1.46
Ti					TiO <sub>2</sub>		Ti	1.69	0.35	1.62	2.82	TiO <sub>2</sub>	0.87
Fe	2.28	0.55	1.86	2.93	FeO	1	Fe	6.14	0.62	5.06	7.9	FeO	2.72
Ce	65.55	1.13	21.3	76.77	Ce <sub>2</sub> O <sub>3</sub>	11.48	Ce	62.21	1.25	20.42	72.86	Ce <sub>2</sub> O <sub>3</sub>	10.99
Th					ThO <sub>2</sub>		Th	0.53	0.84	0.11	0.61	ThO <sub>2</sub>	0.06
0	20.86	0.95	59.36			32	0	20.69	0.98	59.47			32
Totals	100						Totals	100					
					Cation Sum	21.91						Cation Sum	21.81
Anal. No.	3						4						
Anal. No. Element	3 Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	4 Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
Anal. No. Element	3 Weight % 2.33	Weight % Sigma	Atomic %	Compound %	Formula Al <sub>2</sub> O <sub>3</sub>	Number of lons	4 Element	Weight % 7.21	Weight % Sigma	Atomic % 12.57	Compound % 13.62	Formula Al2O3	Number of lons 6.86
Anal. No. Element Al Si	3 Weight % 2.33 0.56	Weight % Sigma 0.41 0.31	Atomic % 4.44 1.02	Compound % 4.4 1.19	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	Number of lons 2.4 0.55	4 Element Al Si	Weight % 7.21	Weight % Sigma 0.56	Atomic % 12.57	Compound % 13.62	Formula Al2O3 SiO2	Number of lons 6.86
Anal. No. Element Al Si P	3 Weight % 2.33 0.56 0.46	Weight % Sigma 0.41 0.31 0.32	Atomic % 4.44 1.02 0.77	Compound % 4.4 1.19 1.06	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> P <sub>2</sub> O <sub>5</sub>	Number of lons 2.4 0.55 0.42	4 Element Al Si P	Weight % 7.21	Weight % Sigma 0.56	Atomic % 12.57	Compound % 13.62	Formula Al2O3 SiO2 P2O5	Number of lons 6.86
Anal. No. Element Al Si P Ca	3 Weight % 2.33 0.56 0.46 2.95	Weight % Sigma 0.41 0.31 0.32 0.31	Atomic % 4.44 1.02 0.77 3.79	Compound % 4.4 1.19 1.06 4.13	Formula $AI_2O_3$ $SiO_2$ $P_2O_5$ CaO	Number of lons 2.4 0.55 0.42 2.05	4 Element Al Si P Ca	Weight % 7.21 2.25	Weight % Sigma 0.56 0.29	Atomic % 12.57 2.64	Compound % 13.62 3.15	Formula Al2O3 SiO2 P2O5 CaO	Number of lons 6.86 1.44
Anal. No. Element Al Si P Ca Ti	3 Weight % 2.33 0.56 0.46 2.95 1.1	Weight % Sigma 0.41 0.31 0.32 0.31 0.35	Atomic % 4.44 1.02 0.77 3.79 1.18	Compound % 4.4 1.19 1.06 4.13 1.83	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> P <sub>2</sub> O <sub>5</sub> CaO TiO <sub>2</sub>	Number of lons 2.4 0.55 0.42 2.05 0.64	4 Element Al Si P Ca Ti	Weight % 7.21 2.25	Weight % Sigma 0.56 0.29	Atomic % 12.57 2.64	Compound % 13.62 3.15	Formula Al2O3 SiO2 P2O5 CaO TiO2	Number of lons 6.86 1.44
Anal. No. Element Al Si P Ca Ti Fe	3 Weight % 2.33 0.56 0.46 2.95 1.1 4.54	Weight % Sigma 0.41 0.31 0.32 0.31 0.35 0.6	Atomic % 4.44 1.02 0.77 3.79 1.18 4.18	Compound % 4.4 1.19 1.06 4.13 1.83 5.84	Formula Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub> P <sub>2</sub> O <sub>5</sub> CaO TiO <sub>2</sub> FeO	Number of lons 2.4 0.55 0.42 2.05 0.64 2.26	4 Element Al Si P Ca Ti Fe	Weight % 7.21 2.25 5.06	Weight % Sigma 0.56 0.29 0.62	Atomic % 12.57 2.64 4.27	Compound % 13.62 3.15 6.52	Formula Al2O3 SiO2 P2O5 CaO TiO2 FeO	Number of lons 6.86 1.44 2.33
Anal. No. Element Al Si P Ca Ti Fe Ce	3 Weight % 2.33 0.56 0.46 2.95 1.1 4.54 68.42	Weight % Sigma 0.41 0.31 0.32 0.31 0.35 0.66 1.36	Atomic % 4.44 1.02 0.77 3.79 1.18 4.18 25.14	Compound % 4.4 1.19 4.13 1.83 5.84 80.14	Formula           Al2O3           SiO2           P2O5           CaO           TiO2           FeO           Ce2O3	Number of lons 2.4 0.55 0.42 2.05 0.64 2.26 13.58	4 Element Al Si P Ca Ti Fe Ce	Weight % 7.21 2.25 5.06 64.49	Weight % Sigma 0.56 0.29 0.62 1.28	Atomic % 12.57 2.64 4.27 21.65	Compound % 13.62 3.15 6.52 75.53	Formula Al2O3 SiO2 P2O5 CaO TiO2 FeO Ce2O3	Number of lons 6.86 1.44 2.33 11.81
Anal. No. Element Al Si P Ca Ti Fe Ce Th	3 Weight % 2.33 0.56 0.46 2.95 1.1 4.54 68.42 1.24	Weight % Sigma           0.41           0.31           0.32           0.31           0.35           0.6           1.36	Atomic % 4.44 1.02 0.77 3.79 1.18 4.18 25.14 0.28	Compound % 4.4 1.19 1.06 4.13 1.83 5.84 80.14 1.41	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 2.4 0.55 0.42 2.05 0.64 2.26 13.58 0.15	4 Element Al Si P Ca Ti Fe Ce Th	Weight % 7.21 2.25 5.06 64.49 1.04	Weight % Sigma 0.56 0.29 0.62 1.28 0.97	Atomic % 12.57 2.64 4.27 21.65 0.21	Compound % 13.62 3.15 6.52 75.53 1.18	Formula Al2O3 SiO2 P2O5 CaO TiO2 FeO Ce2O3 ThO2	Number of lons 6.86 1.44 2.33 11.81 0.12
Anal. No. Element Al P Ca Ti Fe Ce Th O	3 Weight % 2.33 0.56 0.46 2.95 1.1 4.54 68.42 1.24 18.4	Weight % Sigma 0.41 0.32 0.35 0.6 1.36 0.93 1.04	Atomic % 4.44 1.02 0.77 3.79 1.18 4.18 25.14 0.28 59.21	Compound %           4.4           1.19           1.06           4.13           1.83           5.84           80.14           1.41	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 2.4 0.55 0.42 2.05 0.64 2.26 13.58 0.15 32	4 Element Al Si P Ca Ti Fe Ce Th O	Weight % 7.21 2.25 5.06 64.49 1.04 19.95	Weight % Sigma 0.56 0.29 0.62 1.28 0.97 0.97	Atomic % 12.57 2.64 4.27 21.65 0.21 58.66	Compound % 13.62 3.15 6.52 75.53 1.18	Formula Al2O3 SiO2 P2O5 CaO TiO2 FeO Ce2O3 ThO2	Number of Ions 6.86 1.44 2.33 11.81 0.12 32
Anal. No. Element Al Si P Ca Ti Fe Ce Th Ce Th O Totals	3 Weight % 2.33 0.56 0.46 2.95 1.1 4.54 68.42 1.24 18.4 18.4	Weight % Sigma 0.41 0.31 0.32 0.35 0.6 1.36 0.93 1.04	Atomic % 4.44 1.02 0.77 3.79 1.18 4.18 25.14 0.28 59.21	Compound %           4.4           1.19           1.06           4.13           1.83           5.84           80.14           1.41	Formula           Al2O3           SiO2           P2O5           CaO           TiO2           FeO           Ce2O3           ThO2	Number of lons 2.4 0.55 0.42 2.05 0.64 2.26 13.58 0.15 32	4 Element Al Si P Ca Ti Fe Ce Th Ce Th O Totals	Weight % 7.21 2.25 5.06 64.49 1.04 19.95 100	Weight % Sigma 0.56 0.29 0.62 1.28 0.97 0.97	Atomic % 12.57 2.64 4.27 21.65 0.21 58.66	Compound % 13.62 3.15 6.52 75.53 1.18	Formula Al2O3 SiO2 P2O5 CaO TiO2 FeO Ce2O3 ThO2	Number of lons 6.86 1.44 2.33 11.81 0.12 32

Table 10.17e. SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 5). Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anal. No.	1						2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	12.46	0.59	17.85	23.55	Al <sub>2</sub> O <sub>3</sub>	9.75	AI	7.21	0.47	9.33	13.62	Al <sub>2</sub> O <sub>3</sub>	5.2
Ca	2.07	0.26	2	2.9	CaO	1.09	Ca	1.51	0.23	1.32	2.11	CaO	0.73
Ti	1.57	0.33	1.27	2.62	TiO <sub>2</sub>	0.69	Ti	9.41	0.48	6.86	15.7	TiO <sub>2</sub>	3.83
Fe	9.95	0.66	6.89	12.8	FeO	3.76	Fe	30.2	0.88	18.88	38.85	FeO	10.54
Ce	47.29	1.12	13.04	55.39	Ce <sub>2</sub> O <sub>3</sub>	7.13	Ce	24.74	1	6.17	28.98		3.44
Th	2.41	0.85	0.4	2.74	ThO <sub>2</sub>	0.22	Th	0.65	0.74	0.1	0.74	ThO <sub>2</sub>	0.05
0	24.24	0.91	58.56			32	0	26.28	0.88	57.35			32
Totals	100						Totals	100					
					Cation Sum	22.65						Cation Sum	23.8
Anal. No.	3						4						
Anal. No. Element	3 Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	4 Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
Anal. No. Element Al	3 Weight % 15.36	Weight % Sigma	Atomic % 21.37	Compound % 29.02	Formula Al <sub>2</sub> O <sub>3</sub>	Number of lons 11.63	4 Element	Weight % 10.37	Weight % Sigma	Atomic % 15.53	Compound % 19.6	Formula Al <sub>2</sub> O <sub>3</sub>	Number of lons 8.53
Anal. No. Element Al Ca	3 Weight % 15.36 2.45	Weight % Sigma 0.65 0.27	Atomic % 21.37 2.29	Compound % 29.02 3.42	Formula Al <sub>2</sub> O <sub>3</sub> CaO	Number of lons 11.63 1.25	4 Element Al Ca	Weight % 10.37 2.34	Weight % Sigma 0.62 0.29	Atomic % 15.53 2.36	Compound % 19.6 3.28	Formula Al <sub>2</sub> O <sub>3</sub> CaO	Number of lons 8.53 1.3
Anal. No. Element Al Ca Ti	3 Weight % 15.36 2.45	Weight % Sigma 0.65 0.27	Atomic % 21.37 2.29	Compound % 29.02 3.42	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub>	Number of lons 11.63 1.25 2.21	4 Element Al Ca Ti	Weight % 10.37 2.34 1.5	Weight % Sigma 0.62 0.29 0.34	Atomic % 15.53 2.36 1.26	Compound % 19.6 3.28 2.5	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub>	Number of lons 8.53 1.3 0.69
Anal. No. Element Al Ca Ti Fe	3 Weight % 15.36 2.45 6.03	Weight % Sigma 0.65 0.27 0.56	Atomic % 21.37 2.29 4.05	Compound % 29.02 3.42 7.75	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO	Number of lons 11.63 1.25 2.21 7.17	4 Element Al Ca Ti Fe	Weight % 10.37 2.34 1.5 10.95	Weight % Sigma 0.62 0.29 0.34 0.71	Atomic % 15.53 2.36 1.26 7.92	Compound % 19.6 3.28 2.5 14.09	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO	Number of lons 8.53 1.3 0.69 4.35
Anal. No. Element Al Ca Ti Fe Ce	3 Weight % 15.36 2.45 6.03 49.17	Weight % Sigma 0.65 0.27 0.56 1.11	Atomic % 21.37 2.29 4.05 13.17	Compound % 29.02 3.42 7.75 57.59	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO Ce <sub>2</sub> O <sub>3</sub>	Number of lons 11.63 1.25 2.21 7.17 0.17	4 Element Al Ca Ti Fe Ce	Weight % 10.37 2.34 1.5 10.95 49.21	Weight % Sigma 0.62 0.29 0.34 0.71 1.22	Atomic % 15.53 2.36 1.26 7.92 14.19	Compound % 19.6 3.28 2.5 14.09 57.64	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO Ce <sub>2</sub> O <sub>3</sub>	Number of lons 8.53 1.3 0.69 4.35 7.79
Anal. No. Element Al Ca Ti Fe Ce Th	3 Weight % 15.36 2.45 6.03 49.17 1.95	Weight % Sigma 0.65 0.27 0.56 1.11 0.83	Atomic % 21.37 2.29 4.05 13.17 0.32	Compound % 29.02 3.42 7.75 57.59 2.22	$Formula$ $Al_2O_3$ $CaO$ $TiO_2$ $FeO$ $Ce_2O_3$ $ThO_2$	Number of lons 11.63 1.25 2.21 7.17 0.17 32	4 Element Al Ca Ti Fe Ce Th	Weight % 10.37 2.34 1.5 10.95 49.21 2.54	Weight % Sigma 0.62 0.29 0.34 0.71 1.22 0.94	Atomic % 15.53 2.36 1.26 7.92 14.19 0.44	Compound % 19.6 3.28 2.5 14.09 57.64 2.89	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO Ce <sub>2</sub> O <sub>3</sub> ThO <sub>2</sub>	Number of lons 8.53 1.3 0.69 4.35 7.79 0.24
Anal. No. Element Al Ca Ti Fe Ce Th O	3 Weight % 15.36 2.45 6.03 49.17 1.95 25.05	Weight % Sigma 0.65 0.27 0.56 1.11 0.83 0.9	Atomic % 21.37 2.29 4.05 13.17 0.32 58.79	Compound % 29.02 3.42 7.75 57.59 2.22	Formula           Al <sub>2</sub> O <sub>3</sub> CaO           TiO <sub>2</sub> FeO           Ce <sub>2</sub> O <sub>3</sub> ThO <sub>2</sub>	Number of lons 11.63 1.25 2.21 7.17 0.17 32	4 Element Al Ca Ti Fe Ce Th O	Weight % 10.37 2.34 1.5 10.95 49.21 2.54 23.08	Weight % Sigma 0.62 0.29 0.34 0.71 1.22 0.94 0.98	Atomic % 15.53 2.36 1.26 7.92 14.19 0.44 58.28	Compound % 19.6 3.28 2.5 14.09 57.64 2.89	$\begin{tabular}{c} Formula \\ Al_2O_3 \\ CaO \\ TiO_2 \\ FeO \\ Ce_2O_3 \\ ThO_2 \end{tabular}$	Number of lons 8.53 1.3 0.69 4.35 7.79 0.24 32
Anal. No. Element Al Ca Ti Fe Ce Th O Totals	3 Weight % 15.36 2.45 6.03 49.17 1.95 25.05 100	Weight % Sigma 0.65 0.27 0.56 1.11 0.83 0.9	Atomic % 21.37 2.29 4.05 13.17 0.32 58.79	Compound % 29.02 3.42 7.75 57.59 2.22	Formula Al <sub>2</sub> O <sub>3</sub> CaO TiO <sub>2</sub> FeO Ce <sub>2</sub> O <sub>3</sub> ThO <sub>2</sub>	Number of lons 11.63 1.25 2.21 7.17 0.17 32 22.43	4 Element Al Ca Ti Fe Ce Th O Totals	Weight % 10.37 2.34 1.5 10.95 49.21 2.54 23.08 100	Weight % Sigma           0.62           0.29           0.34           0.71           1.22           0.94           0.98	Atomic % 15.53 2.36 1.26 7.92 14.19 0.44 58.28	Compound % 19.6 3.28 2.5 14.09 57.64 2.89	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Number of lons 8.53 1.3 0.69 4.35 7.79 0.24 32

Table 10.17f. SEM semi-quantitative chemical analysis of various spots of a Ce oxide crystal in sample M1 S6 (Crystal 6). Peaks from elements in red color are more likely to come from the background rather than included in the crystals analyzed.

Anal. No.	1						2						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	3.26	0.44	5.82	6.16	Al <sub>2</sub> O <sub>3</sub>	3.25	AI					Al <sub>2</sub> O <sub>3</sub>	
Ca	3.03	0.31	3.64	4.24	CaO	2.04	Ca	3.1	0.3	4.47	4.34	CaO	2.39
Ti	1.17	0.35	1.17	1.94	TiO <sub>2</sub>	0.66	Ti					TiO <sub>2</sub>	
Р					P <sub>2</sub> O <sub>5</sub>		Р	1.22	0.35	2.28	2.8	P <sub>2</sub> O <sub>5</sub>	1.22
F							F						
Si					SiO <sub>2</sub>		Si					SiO <sub>2</sub>	
Fe	14.07	0.77	12.12	18.1	FeO	6.78	Fe	2.54	0.49	2.63	3.27	FeO	1.41
Ce	56.73	1.23	19.49	66.45	Ce <sub>2</sub> O <sub>3</sub>	10.9	Ce	72.85	1.22	30.01	85.32	Ce <sub>2</sub> O <sub>3</sub>	16.09
Th	2.73	0.93	0.57	3.1	ThO <sub>2</sub>	0.32	Th	3.75	0.94	0.93	4.26	ThO <sub>2</sub>	0.5
0	19.01	0.94	57.19			32	0	16.54	0.88	59.68			32
Totals	100						Totals	100					
					Cation Sum	23.95						Cation Sum	21.62
Anal. No.	3						4						
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	6.66	0.52	10.96	12.58	Al <sub>2</sub> O <sub>3</sub>	5.89	AI	4.34	0.48	7.91	8.19	Al <sub>2</sub> O <sub>3</sub>	4.36
Ca	2.87	0.28	3.19	4.02	CaO	1.71	Ca	2.74	0.3	3.37	3.84	CaO	1.86
Ti	4.3	0.41	3.98	7.17	TiO <sub>2</sub>	2.14	Ti	1.41	0.34	1.45	2.35	TiO <sub>2</sub>	0.8
Р					P <sub>2</sub> O <sub>5</sub>		Ρ					P <sub>2</sub> O <sub>5</sub>	
F							F	-0.26	1.19	-0.67	0		-0.37
Si					SiO <sub>2</sub>		Si					SiO <sub>2</sub>	
Fe	4.1	0.56	3.26	5.28	FeO	1.75	Fe	7.34	0.64	6.47	9.44	FeO	3.56
Ce	59.27	1.2	18.79	69.42	Ce <sub>2</sub> O <sub>3</sub>	10.09	Ce	63.03	1.45	22.16	73.82	Ce <sub>2</sub> O <sub>3</sub>	12.19
Th	1.35	0.88	0.26	1.53	ThO <sub>2</sub>	0.14	Th	2.3	0.94	0.49	2.62	ThO <sub>2</sub>	0.27
0	21.45	0.94	59.56			32	0	19.11	0.97	58.82			32.37
Totals	100						Totals	100					
					Cation Sum	21.73						Cation Sum	23.03
Anal. No.				-		5							6
Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons	Element	Weight %	Weight % Sigma	Atomic %	Compound %	Formula	Number of lons
AI	4.8	0.47	8.02	9.06	Al <sub>2</sub> O <sub>3</sub>	4.46	AI	3.46	0.47	6.33	6.53	Al <sub>2</sub> O <sub>3</sub>	3.54
Ca	2.77	0.29	3.12	3.88	CaO	1.74	Ca	2.57	0.3	3.16	3.59	CaO	1.77
Ti					TiO₂		Ti					TiO <sub>2</sub>	
Р					P₂O₅		Р					P <sub>2</sub> O <sub>5</sub>	
F							F						
Si	1.19	0.33	1.92	2.55	SiO <sub>2</sub>	1.07	Si					SiO <sub>2</sub>	
Fe	13.97	0.73	11.3	17.97	FeO	6.28	Fe	13.15	0.75	11.63	16.92	FeO	6.52
Ce	54.79	1.18	17.66	64.18	Ce <sub>2</sub> O <sub>3</sub>	9.81	Ce	60.92	1.23	21.47	71.35	Ce <sub>2</sub> O <sub>3</sub>	12.03
ſh	2.07	0.85	0.4	2.35	IhO₂	0.22	ſh	1.41	0.97	0.3	1.61	IhO <sub>2</sub>	0.17
0	20.4	0.93	57.58			32	0	18.49	0.92	57.1			32
Totals	100			L			Totals	100					
1					Cation Sum	23.57			1			Cation Sum	24.04

Table 10.18. EPMA quantitative chemical analysis of REE bearing minerals at samples M1 S6, M2 S6 and M3 S1. The specific set of elements in the first column was selected and calibrated for analysis in order to be able to identify REE minerals from zircon (Zr, Sc and Hf), anatase/rutile (Ti, Nb and Ta) crystals and bauxite's matrix. Al, Fe, Si, Na, Mg and Mn are the main bauxite elements, while Ca, F, P, Cl, Th, U, REE and Y were chosen for the rare earth crystals analysis. Elements in red colour do not occur in the analyzed crystals because either they are below detection limits or their results are more likely to come from the surrounding area rather than included in crystals. Blue values are very close to the detection limits and are unreliable. Y, Sm, Nd and Gd values in green colour interfere with Ce. Hence, the totals were estimated without including values in red, green and blue colour.

Sample				M1 S6					M2	S6		M3 S1
Comment	M1-1	M1-1	M1-2	M1-3	M1-4	M1-5	M1-6	M2-7	M2-8	M2-9	M2-10	M3-S1
Anal. No.	5	15	6	7	8	9	10	11	12	13	14	16
SiO <sub>2</sub>	2.375	2.397	0.000	0.000	2.520	1.145	2.241	2.081	1.440	1.453	1.129	0.771
Al <sub>2</sub> O <sub>3</sub>	0.259	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
FeO	2.913	2.593	0.000	0.000	3.314	7.077	2.969	9.953	2.138	1.776	0.753	3.404
CaO	3.106	7.295	2.536	2.699	2.856	7.902	7.289	6.101	7.219	6.692	5.772	9.432
Na₂O	-0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
TiO <sub>2</sub>	0.028	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
ZrO <sub>2</sub>	0.092	0.106	0.000	0.000	0.000	-0.044	-0.029	-0.035	0.011	-0.073	-0.029	0.159
HfO <sub>2</sub>	0.158	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
F	1.569	0.000	1.109	0.902	1.111	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$P_2O_5$	0.105	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MgO	-0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MnO	-0.029	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CI	0.043	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nb <sub>2</sub> O <sub>5</sub>	-0.004	0.054	0.000	0.000	0.000	0.039	-0.048	-0.017	-0.026	-0.027	0.064	0.039
Ta <sub>2</sub> O <sub>5</sub>	-0.048	0.020	0.000	0.000	0.000	-0.235	-0.058	-0.433	-0.215	-0.031	-0.058	-0.041
ThO <sub>2</sub>	4.198	4.539	0.000	3.970	4.178	1.588	4.279	-0.097	-0.033	0.029	0.199	0.046
UO <sub>2</sub>	0.193	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sc <sub>2</sub> O <sub>3</sub>	-0.071	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y <sub>2</sub> O <sub>3</sub>	-0.018	-0.037	0.000	0.000	0.000	0.112	-0.014	0.247	0.213	0.144	0.105	0.109
La <sub>2</sub> O <sub>3</sub>	0.064	-0.026	0.000	0.000	0.000	0.000	0.000	0.308	0.073	0.229	0.405	-0.105
	70.399	75.149	66.455	67.451	70.271	58.273	73.310	41.560	65.275	62.797	68.680	68.995
Pr <sub>2</sub> O <sub>3</sub>	-0.180	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nd <sub>2</sub> O <sub>3</sub>	0.896	0.792	0.000	0.000	0.666	0.434	0.569	0.588	0.660	0.659	0.850	0.656
Sm <sub>2</sub> O <sub>3</sub>	0.506	0.588	0.000	0.000	-0.045	0.097	0.669	0.285	0.395	0.330	0.487	0.170
Eu <sub>2</sub> O <sub>3</sub>	0.085	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Gd <sub>2</sub> O <sub>3</sub>	4.467	0.000	0.000	4.029	4.229	4.382	0.000	0.000	0.000	0.000	0.000	0.000
Tb <sub>2</sub> O <sub>3</sub>	0.056	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dy <sub>2</sub> O <sub>3</sub>	-0.399	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ho <sub>2</sub> O <sub>3</sub>	0.211	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Er <sub>2</sub> O <sub>3</sub>	-0.133	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Yb <sub>2</sub> O <sub>3</sub>	0.012	0.155	0.000	0.000	0.000	0.116	0.175	-0.121	-0.026	0.028	0.042	-0.216
Totals	77.703	86.983	68.991	74.120	77.305	67.763	84.878	47.661	72.494	69.489	74.452	78.427



Figure 10.37. EPMA BSE image of a relatively big transferred weathered material fragment, which includes a big Ti-Fe altered crystal and a barite crystal.

## Appendix F: Leaching Methods Summary

Various researchers have suggested leaching techniques, which can be found in the literature. At the moment, the most interesting techniques are precipitation, selective chromatographic separation and liquid emulsion extraction. Additionally, precipitation, liquid-liquid extraction (LLE) and ion exchange (IX) are the most common hydrometallurgical concentration and purification methods, used in the mining industry today. Precipitation and electrolysis are also used quite often but as the final recovery step.

Generally, REE are difficult to separate from each other due to their chemical similarities. The solubility of salts, the hydrolysis of ions, and the formation of complex species are controlled by the difference in basicity of REE. Therefore, separation processes such as fractional precipitation, ion exchange, and solvent extraction are based on these properties (Gupta, 1992). Selective oxidation or reduction can be used to simplify the separation of some of the REE.

1) Precipitation: In this method, rare earths are stripped from loaded solvent extractants by using aqueous solutions of inorganic acids. The dissolved rare earths are then precipitated as insoluble oxalates and carbonates (oxide precursors), from which oxides are recovered by calcination (Konishi and Noda, 2001). The stripping and precipitation steps can also be combined (Konishi and Noda, 2001; El-Hefny et al. 2010). More precisely, rare earth metals can be separated from other metals in a weakly acidic medium (pH 1 - 4) by precipitating as oxalates with oxalic acid, since many other metals (e.g. Fe, Al, Ti, Zr, Nb, and Mo) remain in solution as soluble oxalate complexes. Individual REE in high purity have also been produced by separation as double nitrates. The separation is more sensitive for the LREE since the property difference between rare earths decreases as the atomic number increases. One of the most widely used precipitation method to separate REE from acidic by precipitation of sodium double solutions is sulphate hydrates  $(NaRE(SO_4)_2.xH_2O)$  through the addition of sodium sulphate (Gupta 1992).

2) Solvent Extraction: This technique is well known and widely used. The metal ion solution is mixed with an organic solvent. Extractant chemicals in organic phase are used to improve the transfer of the metal ions into the

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organic phase. Liquid-liquid extraction is still used to separate rare earth metals from different leach solutions on industrial scale. However, the separation of adjacent rare earth metals by using conventional extraction system is still difficult, because such extractive separation processes are based on only the differences in the complex formation ability between the rare earth metals and their extractant (Nishihama, 2003). Another limitation in traditional solvent extraction is the need of large volumes of organic solvents, which is not environmentally friendly.

*3) Liquid Emulsion Membranes Extraction:* This method is based on the formation of a stable emulsion between two immiscible phases. Then the emulsion is dispersed into a third continuous phase by agitation. More precisely:

- The organic membrane phase consists of an organic solvent that contains an extracting agent and an emulsifier.
- The internal aqueous phase (droplets) contains a stripping agent.
- The external continuous phase is the aqueous feed solution containing the species to be extracted.

The target species can then be recovered from the aqueous feed into the organic phase and then stripped into aqueous droplets in the emulsion. The emulsion is broken by typically electrostatic coalescence and then the target species can be recovered by electrowinning or precipitation (Hasan et al., 2009). The extraction chemistry is essentially the same as in liquid-liquid extraction (LLE). Additional attractive features of LEM extraction, compared to LLE, are high selectivity and simple and continuous operation. At the moment, this technique is not fully developed and more research is needed before large scale and wide spread application in industry can occur. Despite the fact that many metal ions have been extracted successfully by this method, only a few papers have reported the same for REE (Kakoi et al., 1997; Hasan et al., 2009).

4) Chromatographic separation: Chromatographic separations by molecular recognition systems are designed to bind selectively with ions based on several parameters such as size, coordination chemistry and geometry and thus exhibit high selectivity. Metal separations at mg/L or lower levels that are not possible using traditional technologies can be achieved using these selective chromatographic systems. Izatt et al. (2010) suggested that there are attractive possibilities for applying molecular recognition technology to REE

recovery from low level wastes and end-of-life products. Ion imprinted polymers have been investigated for selective separation and pre-concentration of rare earth metals. Adsorbents such as Ce (III) (Zhang et al., 2010), La(III) (Li and Sun, 2007) and Nd(III) (Park and Tavlarides, 2010) have been synthesized.









Figure 10.39. Diagrams showing the behavior of trace elements with depth in Mine 1 Profile 2.



Figure 10.40. Diagrams showing the behavior of trace elements with depth in Mine 2 Profile 1.



Figure 10.41. Diagrams showing the behavior of trace elements with depth in Mine 2 Profile 2.



Figure 10.42. Diagrams showing the behavior of trace elements with depth in Mine 3 Profile 1.



Figure 10.43. Diagrams showing the behavior of trace elements with depth in Mine 3 Profile 2.



Figure 10.44. Diagrams showing the behavior of trace elements with depth in Mine 4 Profile 1.



Figure 10.45. Diagrams showing the behavior of trace elements with depth in Mine 4 Profile 2.



Figure 10.46. Chondrite normalized (McDonough and Sun, 1995) REE patterns for various ophiolite related rocks of Pindos ophiolites that are likely to be genetically associated to bauxites.



Figure 10.47. Chondrite normalized (McDonough and Sun, 1995) REE patterns for various ophiolite related rocks of Othris ophiolites that are likely to be genetically associated to bauxites.



Figure 10.48. Chondrite normalized (McDonough and Sun, 1995) REE patterns for various ophiolite related rocks of Othris ophiolites that are likely to be genetically associated to bauxites.



Figure 10.49. Chondrite normalized (McDonough and Sun, 1995) REE patterns for various ophiolite related rocks of Iti and Kallidromon ophiolites that are likely to be genetically associated to bauxites.



Figure 10.50. Chondrite normalized (McDonough and Sun, 1995) REE patterns for various amphibolites of Euboea that are likely to be genetically associated to bauxites.



Figure 10.51. Chondrite normalized (McDonough and Sun, 1995) REE patterns for the Marmeiko laterites that are likely to be genetically associated to bauxites.