

# Rare earth elements and scandium mineralogy in bauxite residue

Johannes VIND<sup>1,2</sup>, Vicky VASSILIADOU<sup>1</sup>, Dimitrios PANIAS<sup>2</sup>

<sup>1</sup> Department of Continuous Improvement and Systems Management, Aluminium of Greece plant, Metallurgy Business Unit, Mytilineos S.A., Agios Nikolaos, 32003 Boeotia, Greece

<sup>2</sup> School of Mining and Metallurgical Engineering, National Technical University of Athens, Iroon Polytechniou 9, 15780, Zografou Campus, Athens, Greece

*johannes.vind@alhellas.gr, vicky.vassiliadou@alhellas.gr, panias@metal.ntua.gr*

## Abstract

*The purpose of the present work was to elucidate the mineralogical nature of rare earth elements (REE) and scandium (Sc) in bauxite residue (BR). It was found that REEs occur in BR in discrete mineral particles. REE-containing particles consist also of titanium (Ti) and iron (Fe), thus they were termed as REE ferrotitanates. REE ferrotitanates were found to form a solid solution between the ideal end-members  $(REE, Ca, Na)(Ti, Fe)O_3$  and  $(Ca, Na)(Ti, Fe)O_3$ . In BR, Sc was found to be present in hematite, goethite and zircon as a trace impurity. Sc does not occur in other BR minerals or does so in a very low concentration; neither does Sc occur in discrete mineral forms. The results of this work showed, that despite the known similarities of REEs and Sc, they do not occur in similar mineral forms in BR.*

## Introduction

The rare earths market is suffering from a scarcity of sources, fluctuations in the prices, export quotas, underdeveloped recycling technologies and the *balance problem*.<sup>1</sup> Besides, the largest rare earth mines are operating with a major ecological impact.<sup>2</sup> These issues are a challenge in the context of responsible sourcing of rare earth elements<sup>3</sup> and alternatives for current practices are necessary.

Bauxite residue (BR) is often considered as a prospective secondary resource of rare earth elements (REE) as well as scandium (Sc).<sup>3-5</sup> Technologies aiming for the extraction of these metals from BR are continuously being developed and improved.<sup>4,6</sup> Even though the knowledge about the mineralogy of any raw material is crucial for an extractive metallurgy project, little is reported about the mineralogical occurrence of REEs and Sc relating to BR.<sup>5</sup> This contribution aims to bring new knowledge to the topic based on electron microprobe analysis of BR, and comparison is made with reports from the literature. In the present work, we discuss the REEs (lanthanides and yttrium) separately from Sc to emphasise their contrasting occurrence forms in BR.

## Materials and Methods

Currently discussed BR sample is collected from Aluminium of Greece, Metallurgy Business Unit, Mytilineos S.A. (AoG).

Chemical composition of the studied sample was determined by the X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) methods. Bulk mineralogical composition was determined by X-ray diffraction (XRD). Microscale analysis was performed by electron probe microanalysis coupled with wavelength dispersive spectroscopy (EPMA-WDS) by using a JEOL JXA-8530F instrument. Appropriate standards were used to calibrate the WDS measurements.

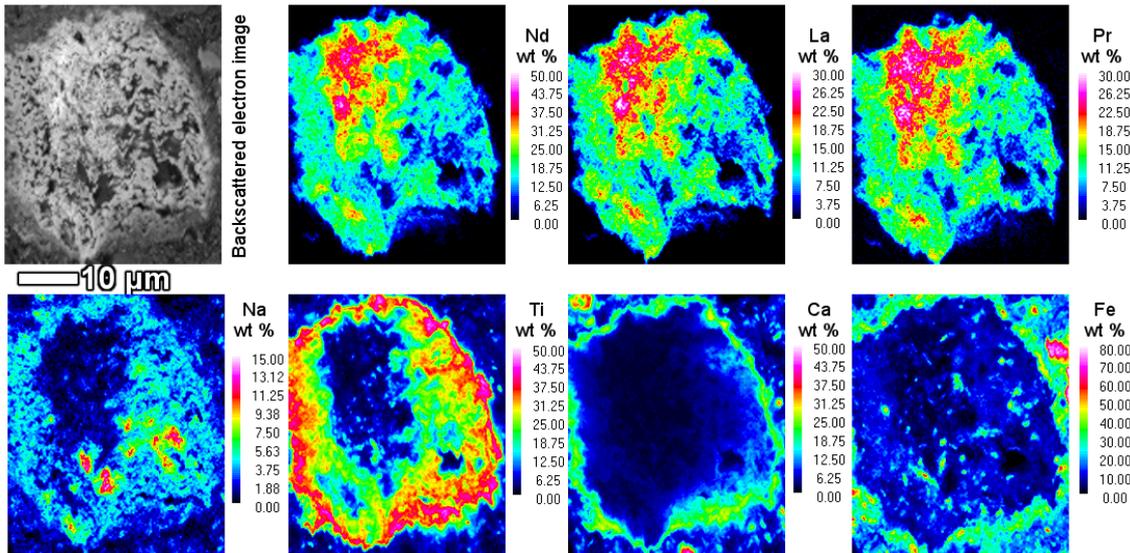
## Results and Discussion

### Bulk composition

The studied BR sample was composed of Fe<sub>2</sub>O<sub>3</sub> (41.7 wt%), Al<sub>2</sub>O<sub>3</sub> (20.6 wt%), CaO (10.7 wt%), SiO<sub>2</sub> (6.8 wt%), TiO<sub>2</sub> (5.3 wt%), Na<sub>2</sub>O (2.9 wt%), determined by XRF. Additional 9.2 wt% of the mass was attributed to the loss on ignition. The main mineral phases determined by XRD in the sample were hematite, hydrogarnet, diaspore, cancrinite, goethite, and perovskite. Total REEs concentration of the sample, analysed by ICP-MS, including the lanthanides, yttrium and scandium, was 1093 mg/kg.

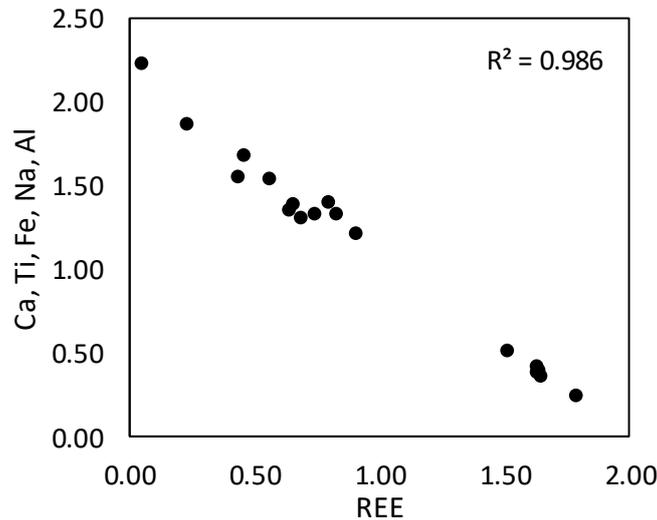
### Rare Earth Element Phases in Bauxite Residue

Rare earth element phases can be found in BR in discrete mineral particles, as seen from an example on Figure 1. These mineral particles have substantially higher REE concentration compared to the bulk concentration of REEs in bauxite residue. It can be suggested from the presence of titanium, iron and especially sodium within this (Figure 1) and similar grains, that Bayer process has changed the form of how REEs occur in BR compared to the initial REE phases in bauxite. In bauxite, REEs occur mainly as fluorocarbonate and phosphate species.<sup>7</sup> The chemical composition of the particle on Figure 1 changes from the core to the rim of the particle, indicating to the reaction that has occurred between the particle and Bayer processing liquor. It seems that the core of the particle has not been affected by the reaction. On the outer part of the particle, a shell composed of calcium ferrotitanate can be discerned.



**Figure 1.** EPMA-WDS quantitative elemental mapping of a REE particle that has been affected by the Bayer process

Due to the clear presence of Ti and Fe in the reacted REE particles they can be termed as REE ferrotitanates. An  $ABX_3$  perovskite structure is assumed as a best fit for such chemical composition, where A is a relatively large cation (REE, Ca, Na), B is a relatively small cation ( $Fe^{3+}$ , Ti) and X is oxygen.<sup>8</sup> A high content of REEs in the observed grains goes hand in hand with a low Ca, Ti, Fe, Na and Al content and vice versa (Figure 2). This suggests the existence of a solid solution character of the REE ferrotitanate phases.



**Figure 2.** Ionic proportions of the cations in REE ferrotitanate particles, calculated based on  $ABX_3$  structure from EPMA-WDS quantification results

It can be concluded from Figure 1 as well as Figure 2, that REE ferrotitanates occur as a solid solution between the ideal end-members  $(\text{REE,Ca,Na})(\text{Ti,Fe})\text{O}_3$  and  $(\text{Ca,Na})(\text{Ti,Fe})\text{O}_3$  in BR.

Minor amounts of REEs are found in BR as phosphate phases, namely as cerium and yttrium phosphates. The presence of REE phosphates in BR indicates that these minerals, originally found in bauxite ore,<sup>9</sup> endure partly the Bayer process conditions.

The very scarce mentions of REE mineralogy relating to BR in the literature have briefly mentioned the co-occurrence of REEs or a particular REE with Ti.<sup>10-12</sup> This indicates that present observations point to a wider phenomenon of REE occurrences in BR that is not isolated only for the case of AoG's BR. Current work does not provide any supporting or contradictory evidence for the suggestion that REEs might be incorporated into the structure of hematite in BR.<sup>13</sup>

### **Scandium Occurrence Forms in Bauxite Residue**

Bauxite residue particles were examined with EPMA-EDS to identify the carrier minerals of Sc. It was discerned that iron oxide predominant particles, corresponding to hematite and goethite, are the main hosts of Sc in BR (Table 1). Hematite contains 190 mg/kg Sc on average, goethite 330 mg/kg Sc on average, while a certain population of hematite particles is Sc-depleted (Table 1). Zircon grains were found to contain about 5000 mg/kg Sc (based on 6 measurements) in their composition. Other BR mineral constituents like diaspore, cancrinite, perovskite and hydrogarnet did not contain or contained a very small quantity of Sc.

### **Conclusions**

There is a clear distinction between the mineralogical occurrence form of Sc and REEs contained in BR. Sc is always found as a trace element associated with hematite and goethite in BR while REEs appear in discrete phases. Sc occurrence in BR from RUSAL Urals refinery in Russia is somewhat contrasting compared to BR from AoG, where about 65% of Sc is thought to appear in an easily extractable adsorption form on the surface of BR particles.<sup>14</sup> In smaller proportions, Sc content is reported to be in chamosite in the Urals BR.<sup>14</sup> Thus, the occurrence forms of Sc in different BRs can be rather diverse.

**Table 1.** Sc concentration in iron oxide matrixes of BR, measured by EPMA-WDS

	Hematite (n = 24)		Sc-depleted hematite (n = 32)		Goethite (n = 10)	
	Average	±	Average	±	Average	±
Fe <sub>2</sub> O <sub>3</sub> (wt%)	92.02	4.06	93.81	3.49	85.89	4.84
TiO <sub>2</sub> (wt%)	3.98	2.17	1.02	0.82	2.36	3.34
Al <sub>2</sub> O <sub>3</sub> (wt%)	1.79	0.60	1.91	1.47	0.75	0.72
SiO <sub>2</sub> (wt%)	0.71	0.60	1.11	0.68	1.84	0.43
Na <sub>2</sub> O (wt%)	0.29	0.26	0.43	0.27	0.36	0.23
CaO (wt%)	0.49	0.32	0.44	0.17	0.29	0.20
Cr <sub>2</sub> O <sub>3</sub> (wt%)	0.24	0.12	0.05	0.05	0.05	0.04
V <sub>2</sub> O <sub>3</sub> (wt%)	0.17	0.11	0.07	0.12	0.05	0.03
Sc (mg/kg)	190	70	30	20	330	240
Total (wt%)	99.74	3.39	98.99	2.28	91.73	3.15

## Acknowledgements

We would like to thank Annelies Malfliet, Bart Blanpain, István Sajó and Alan H. Tkaczyk, who have contributed to the completion of this work. The research leading to these results has received funding from the European Community's Horizon 2020 Programme (H2020/2014-2019) under Grant Agreement no. 636876 (MSCA – ETN REDMUD). This publication reflects only the authors' views, exempting the Community from any liability. Project website: <http://www.etn.redmud.org>.

## References

1. K. Binnemans, P. T. Jones, Rare earths and the balance problem, *J. Sustain. Metall.*, **1**(1), 29-38, 2015.
2. S. H. Ali, Social and environmental impact of the rare earth industries, *Resources*, **3**(1), 123-34, 2014.
3. F. Wall, A. Rollat, R. S. Pell, Responsible sourcing of critical metals, *Elements*, **13**(5), 313-318, 2017.
4. K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Pontikes, Towards zero-waste valorisation of rare-earth-containing industrial process residues: A critical review, *J. Clean. Prod.*, **99**, 17-38, 2015.
5. C. R. Borra, B. Blanpain, Y. Pontikes, K. Binnemans, T. Van Gerven, Recovery of rare earths and other valuable metals from bauxite residue (red mud): A review, *J. Sustain. Metall.*, **2**(4), 365-86, 2016.
6. K. Evans, The history, challenges, and new developments in the management and use of bauxite residue, *J. Sustain. Metall.*, **2**(4), 316-331, 2016.
7. É. A. Deady, E. Mouchos, K. Goodenough, B. J. Williamson, F. Wall, A review of the potential for rare-earth element resources from European red muds: Examples from Seydişehir, Turkey and Parnassus-Giona, Greece, *Mineral. Mag.*, **80**(1), 43-61, 2016.
8. R. H. Mitchell, M. D. Welch, A. R. Chakhmouradian, Nomenclature of the perovskite supergroup: A hierarchical system of classification based on crystal structure and composition, *Mineral. Mag.*, **81**(3), 411-461, 2017.

9. M. Laskou, G. Andreou, Rare earth elements distribution and REE-minerals from the Parnassos-Ghiona bauxite deposits, Greece, in *Mineral Exploration and Sustainable Development*, 7th Biennial SGA Meeting, 89-92, Athens, Greece, 2003.
10. P. N. Gamaletsos, A. Godelitsas, T. Kasama, A. Kuzmin, M. Lagos, T. J. Mertzimekis, J. Göttlicher, R. Steininger, S. Xanthos, Y. Pontikes, G. N. Angelopoulos, C. Zarkadas, A. Komelkov, E. Tzamos, A. Filippidis, The role of nano-perovskite in the negligible thorium release in seawater from Greek bauxite residue (red mud), *Sci. Rep.*, **6**, 1-13, 2016.
11. K. Sugita, Y. Kobayashi, Y. Taguchi, S. Takeda, Y. Ota, M. Ojiri, K. Oda, H. Sano, Method of recovering rare-earth elements, patent no. US20150086449 A1, 2015.
12. S. Reid, J. Tam, M. Yang and G. Azimi, Technospheric Mining of Rare Earth Elements from Bauxite Residue (Red Mud): Process Optimization, Kinetic Investigation, and Microwave Pretreatment, *Sci. Rep.*, **7** (1), 1-9, 2017.
13. R. M. Bolanz, S. Kiefer, J. Göttlicher, R. Steininger, Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) – A potential Ce<sup>4+</sup> carrier in red mud, *Sci. Total Environ.*, **622–623**, 849-60, 2018.
14. A. Suss, N. V. Kuznetsova, A. Kozyrev, A. Panov, S. Gorbachev, Specific features of scandium behavior during sodium bicarbonate digestion of red mud, in *Travaux No. 46*, 491-504, 35th International ICSOBA Conference, Hamburg, Germany, 2017.