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Characterization of scandium and gallium in red mud with Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) and Electron Probe Micro-Analysis (EPMA)

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ABSTRACT

Red mud is a kind of by-product generated in alumina production and typically contains some rare metals like Sc and Ga. In this study, Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) and Electron Probe Micro-Analysis (EPMA) were used to investigate the affinities of Sc and Ga with the major elements including Fe, Al, Si, Ti and Ca existed in red mud. Combined the mapping analyses of high mass resolution of ToF-SIMS with individual spot and mapping analyses of EPMA, the substitution of scandium and gallium for these major elements should follow the order of Ti > Fe > Al > Si and Fe > Al > Ti > Ca > Si, respectively. Scandium has an apparent enrichment in the mineral phases of anatase, hematite and goethite. The hetero-valent isomorphism of $4Sc^{3+} \rightarrow 3Ti^{4+}$ plays a critical role in substitution of Sc^{3+} into the anatase structure and is different from that of $Sc^{3+} \rightarrow Fe^{3+}$ occurred in hematite or goethite. Part of scandium is also found to be existed in silicon-rich minerals of quartz or zeolite. Gallium is closely coordinated with ferrum and aluminum, suggesting that it can proxy for these elements in the crystal lattices of hematite, goethite and gibbsite. All the observations are fundamental clues to the extraction technology of scandium and gallium from red mud.

1. Introduction

The cut-off grade of scandium-containing ore for commercial exploitation is 20 parts per million (ppm) pointed by Liu and Li (2015) and Shaoquan and Suqing (1996). Bauxite in general contains scandium and gallium in trace level. After being subjected to the Bayer process, scandium remained in the bauxite residue, namely red mud, can be beneficiated to approximately two times as much as the concentration of that in bauxite (Akinci and Artir, 2008; Kinnarinen et al., 2015; Ochsenkühn-Petropoulou et al., 2002; Onghena et al., 2017). As for the gallium, nearly 30% of which could still exist in that residue (Liu and Li, 2015). Thus, Bayer red mud is a potential valued solid waste for the extraction of these precious metals.

In particular, the price of scandium ingot with 99.9% purity and Sc_2O_3 with 99.99% purity (4N) could reach to 134 US$ g^{-1} and 5.10 US$ g^{-1} in 2015, respectively (Ober and Jaskula, 2016). Some other information about the price change of Sc_2O_3 and Ga is exhibited in Fig. 1(Cordier and Jaskula, 2011; Ober and Jaskula, 2016). It can be observed that there is a gradual decline in the price of Ga from 2011, while the price of Sc_2O_3 shows a steep increase from the same year. Despite scandium's stiff price and scarcity, multiple potential high-value commercial applications for the metal have been developed over the past two decades. Of particular interest is the addition of scandium into various aluminum alloys, which could make the products like high-end sport and aerospace equipment much stronger, lighter, more heat and corrosion resistant, and also more weldable. Besides, scandium can be applied in solid oxide fuel cells (SOFCs) for excellent electrical conductivity and heat stabilization qualities (Irvine et al., 2005).

So far the affinities of these elements with the others are still poorly understood. This is owing to the tiny amounts of scandium and gallium in the red mud, it is difficult to ascertain their affinities through the conventional test methods, such as X-ray diffraction (XRD), X-ray

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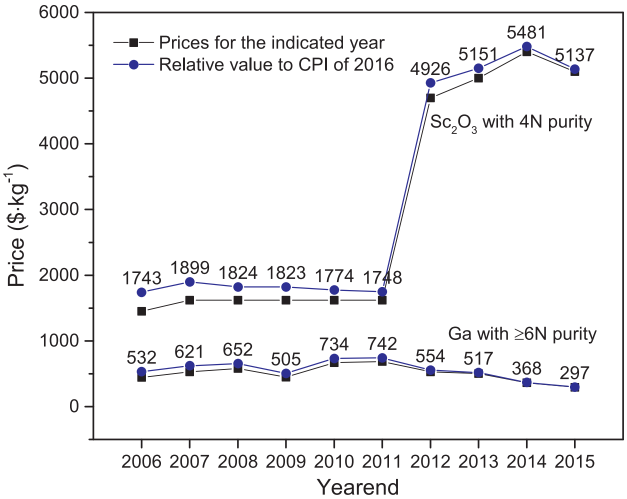

Fig. 1. Prices of products of 6N Ga and 4N Sc_2O_3 in recent ten years.

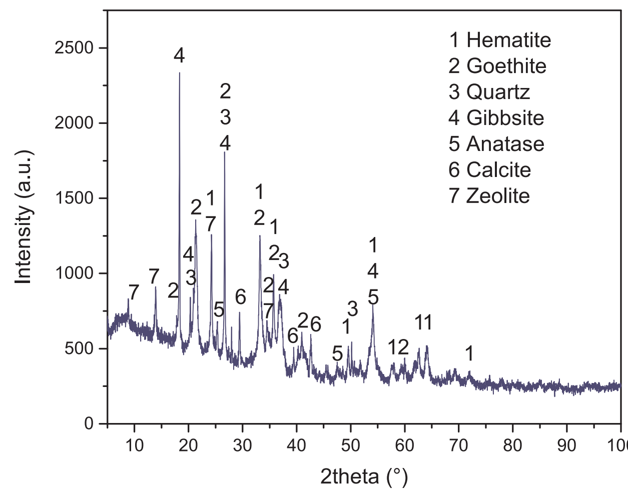

Fig. 2. X-ray diffraction pattern of Bayer red mud.

photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS). X-ray absorption spectroscopy (XAS) is a powerful technique for its sensitivity to the local structure and can be exploited for exploring the speciation of elements (Burke et al., 2012; Gamaletsos et al., 2016; Lockwood et al., 2014). Take arsenic for example, it has been widely examined by K-edge XANES and EXAFS spectra and proved that it appears as As^{5+} in form of arsenate (Burke et al., 2012; Lockwood et al., 2014). Of note, the calculation and fitting of these spectra are complicated. However, never before had somebody carried out the characterization of scandium and gallium in red mud with the analysis of Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS) and Electron Probe Micro-Analysis (EPMA), particularly by the former detection technique.

ToF-SIMS is a surface sensitive analytical technique allowing for local ions detection with a high sensitivity and in-depth resolution (less than 2 nm), which can provide chemical and distributional information for multifarious materials. The analytical capabilities of ToF-SIMS include trace element detection limits in the ppm range (Sodhi, 2004). That analytical technique for the research of archeological ceramic materials is well known. For instance, Tognazzi et al. (2011) have succeeded in characterizing the ancient ceramic impasto on the chemical composition and distributional features with the aid of ToF-SIMS results. Besides, this technique is particularly suitable for precious sample since its non-destructive analysis. The structurally bound hydroxyl in fluorapatite grains from Apollo 15 Mare basalt 15058, 128 has been first discovered by ToF-SIMS (McCubbin Francis et al., 2010). Very few data, except Abhilash et al. (2014) suggest that lanthanum and cerium exhibit a sporadic distribution in the red mud, have been published on the characterization of trace elements by EPMA.

The occurrence mode characteristics of scandium and gallium in the red mud are critical to the choosing of recovery methods and are of help to the development of other recovering methods or practical complex utilization techniques. The aim of this paper was to clarify the main host minerals for Sc and Ga and their distributional features among the major elements, namely Fe, Al, Si, Ti and Ca, by analyzing the element mappings and spot chemical analyses of Fe-, Al-, Si-, Ti- and Ca-rich areas via ToF-SIMS/EPMA.

2. Experimental procedure

Red mud was provided by an aluminum plant of Chalco located in Shangdong province of China. The major chemical composition was determined by X-ray fluorescence (XRF-1800, RIGAKU, Japan) and trace elements of scandium and gallium by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Optima 7000DV, Perkin Elmer, USA) after digesting the red mud with $HCl-HNO_3-HF-HClO_4$ system according to the ASTM standard E2941-14 (ASTM International, 2014). The mineral phases of red mud were investigated by powder X-ray Diffraction (XRD, SmartLab, Rigaku, Japan) with a 2θ scan range of 5–100° and a speed of 10° min^{-1}.

In the present study, the samples for ToF-SIMS observation (TOF. SIMS 5, ION-TOF GmbH, Germany) were prepared in two different ways, i.e. embedding the red mud powder in the indium foil directly (like an indium-powder-indium sandwich) and organizing in an epoxy mount (E-44). For the former method, the red mud was first sprinkled onto a thick indium foil (12 mm × 12 mm × 0.1 mm, 5N purity); then placed the other indium foil over the powder and pressed the sandwich; finally, peeled off the foils and blown off the loose powder. The latter sample was prepared as standard geological thin section in a size of 46 mm × 27 mm × ~0.3 mm (without the thickness of cover slip). The working surface was ground with SiC paper (≥1200 grit finish) and polished with ≤6 μm diamond paste. Subsequently, sample obtained was cut into square shape with ~15 mm × ~15 mm and then washed

Table 1
Major chemical compositions of red mud tested by XRF in wt.% and trace elements by ICP-OES.

Oxides	Al_2O_3	CaO	Fe_2O_3	Na_2O	SiO_2	TiO_2	SO_3	Ga/g t^{-1}	Sc/g t^{-1}	Others
Content	22.753	2.556	38.203	12.254	19.029	3.275	0.990	920 ± 10	80 ± 10	0.94

Notes: Others include the minor components with concentration less than 0.5 wt%, such as Cl, Cr_2O_3, K_2O, MgO, MnO, Nb_2O_5, P_2O_5, SrO, ZnO and ZrO_2.