

Micro-scale ($\sim 10 \mu\text{m}$) analyses of rare earth elements in silicate glass, zircon and apatite with NanoSIMS



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ARTICLE INFO

Article history:

Received 3 April 2016

Received in revised form 11 June 2016

Accepted 13 June 2016

Available online 24 June 2016

Keywords:

Rare earth element

NanoSIMS

Apatite

Zircon

Silicate glass

ABSTRACT

Micron-scale ($\sim 10 \mu\text{m}$) analyses of rare earth elements (REEs) in silicate glass, zircon and apatite were carried with nano-scale secondary ion mass spectrometer (NanoSIMS) operating at high mass resolution mode ($m/\Delta m \sim 10000$, 10%), which eliminating isobaric interferences of heavy REEs by light REE monoxides. To achieve high lateral resolution, the primary O^- probe was optimized to a current of $\sim 1 \text{ nA}$ and a diameter $< 2.5 \mu\text{m}$, scanning over the analysis area of $5 \times 5 \mu\text{m}^2$ or $10 \times 10 \mu\text{m}^2$. The analyses were conducted at a combined mode of multi-collection and peak-jumping to improve the analytical efficiency. Fifteen ion species including rare earth elements and a reference element (Si or Ca) were counted through 4 times of magnetic field switch. The standards of NIST glass, apatite and zircon were analyzed in this study, which represent flat patterns, LREE-enriched and LREE-depleted and show different matrix effects. The relative sensitivity factors (RSF) of REEs are higher in zircon than NIST glass by a factor of 20–50% referred to $^{30}\text{Si}^+$, and they are higher in apatite than NIST glass by a factor of 2–3 referred to $^{42}\text{Ca}^+$. Therefore, the absolute concentration of REEs could be only calibrated with the matrix-matched mineral standards in the SIMS analysis. The analytical reproducibilities (1SD) were $< 5\%$ for silicate glass (NIST SRM 610), $< 10\%$ for apatite (Durango) and $< 15\%$ for zircon (M257). The analytical accuracies determined from the measurements of the standards NIST glass (NIST SRM 612), apatite (MAD and Otter lake) and zircon (91500) were better than 10%, 20% and 30%, respectively, except for La interfered by ZrSiO and ZrO_3 for zircon.

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Abundance patterns of the rare-earth elements (REEs) in minerals are important to probe processes of magmatism and/or crystallization [1–4], e.g. positive or negative deviation of europium from chondrite-normalized abundance patterns is particularly effective in petrogenetic modeling [5,6]. Normally, microanalyses of REEs were performed by laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS) [7–9] and secondary ion mass spectrometry (SIMS) [10–15]. Compared with LA-ICP-MS, SIMS analyses were severely affected by overlapping of light REE (LREE) mono-oxides onto heavy REEs (HREEs). On the other hand, technology of SIMS provides a better lateral resolution ($< 30 \mu\text{m}$) and better depth resolution than LA-ICP-MS [10,11]. Furthermore, trace elements can be measured with a lateral resolution of $< 10 \mu\text{m}$ using NanoSIMS, which is important for compositionally zoned zircons [16–18] and extraterrestrial grains, e.g. from the Moon, Mars and other types of meteorites [15,19,20]. Hofmann et al. (2009,2014) reported measurements of trace elements in zircons of $\sim 1 \mu\text{m}$

using NanoSIMS, but only Y and Ce were analyzed. There are few analyses of all REEs carried out with a lateral resolution of $< 10 \mu\text{m}$.

There are technical difficulties in measuring of all the REEs with NanoSIMS, especially isobaric interferences of HREEs by LREE mono-oxides and long-time counting. In order to reduce or remove the LREE mono-oxide interferences, the energy filtering technique is commonly used [10,12–14]. However, energy filtering causes a significant loss of secondary ion transmission (two orders of ion intensity). In addition, about 40 secondary ions need to be counted, in order to resolve REEs from possible interferences [13–15]. The mass resolving power of new generation SIMS (e.g. IMS 1280 and SHRIMP) is high enough to separate LREE mono-oxides from HREEs. However, these REEs measurements were conducted mono-collector mode, and they were time-consuming because of switching the magnetic field at least 15 times in order to count all 14 REEs plus a reference element.

In order to meet the requirement of high lateral resolution ($\leq 10 \mu\text{m}$) analysis of REEs, we developed a new method using NanoSIMS 50L. The measurements were conducted at high mass resolution mode ($M/\Delta M$: ca.10000), with 14 REEs and one reference element integrated in a combined multi-collection and peak

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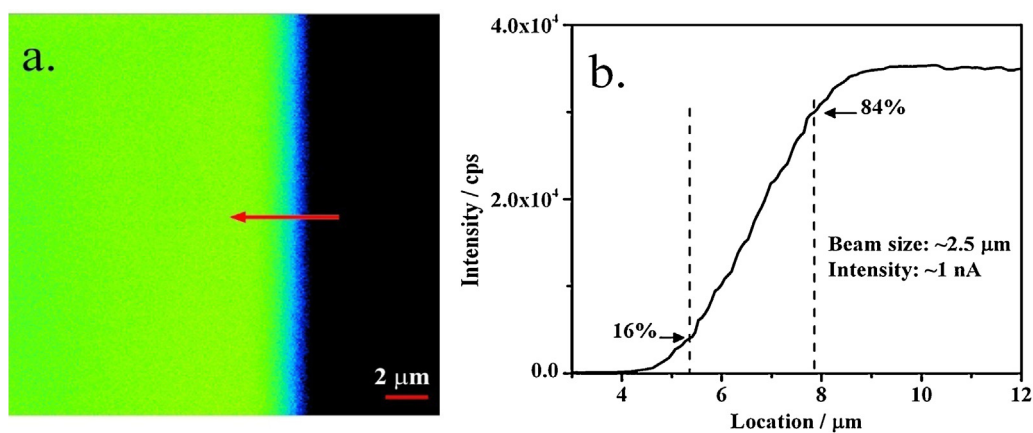


Fig. 1. (a) ^{31}P image of the boundary between apatite and carbonate acquired with a $^{16}\text{O}^-$ beam of ~ 1 nA. (b) Line-profile of ^{31}P ion intensity along the red arrow in (a). The size of the primary beam was measured to be ~ 2.5 μm by the knife-edge method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

jumping mode. The new method eliminates isobaric interferences of HREEs by LREE monoxides and significantly improves the analytical efficiency by reducing peak jumping to only 4 times. The standards of NIST glass, apatite and zircon were analyzed in this study, which represent flat patterns, LREE-enriched and LREE-depleted and show different matrix effects.

1. Sample description

In order to investigate matrix effects of different minerals and to estimate isobaric interferences of HREEs by LREE monoxides of samples with different REE patterns, three types of samples, i.e. silicate glass (flat REE pattern), apatite (LREE-enriched) and zircon (LREE-depleted), were selected. The samples are NIST glass standards SRM 610 and 612, zircon standards M257 and 91500, and apatite standards Durango, Madagascar and Otter Lake. The concentrations of REEs of the standard samples were summarized in Table 1. NIST 612 and the zircon standards were embedded in epoxy resin and made into a polished disk with a diameter of ~ 25.4 mm. NIST 610 and the apatite standards were embedded in another polished disk with a diameter of ~ 12.7 mm. Both polished disks were coated with gold.

1.1. Silicate glass

Both NIST SRM 610 and 612 glass wafers, produced by the National Institute of Standards and Technology (NIST), are widely used as reference materials for trace element measurements with micro-analytical techniques [9,21–24]. The concentration of trace elements in NIST SRM 610 and 612 have been measured with various methods, e.g. ID-TIMS, ICP-MS, LA-ICP-MS and SIMS [21,23,25–27], and the updated values [21] are adopted in this study.

1.2. Apatite

Durango apatite is a distinctive yellow-green fluorapatite found as exceptionally coarse crystals within an open pit iron mine at Cerro de Mercado, on the northern outskirts of Durango City, Mexico. Its chemical composition was determined with ICP-MS and later was demonstrated homogenous suitable for microanalysis of U-Pb dating, Sm-Nd isotopes and trace elements [28–31]. Madagascar apatite is a large fragment of a blue gem quality apatite crystal from the 1st Mine Discovery in Madagascar [28,29,32]. Otter Lake apatite was sampled from Otter Lake area, Québec, Canada, which locates north Bancroft domain within the Grenville Province [33].

The REEs concentrations of MAD and Otter Lake were determined with LA-ICP-MS recently [28].

1.3. Zircon

The 91500 and M257 zircons were well-known standards for in-situ microanalysis of U-Pb dating. The 91500 zircon is a fragment of a single crystal from Kuehl Lake, Ontario, Canada, and the trace element concentrations were determined with LA-ICP-MS in several labs [8,34]. The M257 zircon was an oval shaped, gem-quality crystal from the Ratnapura district, Sri Lanka. The trace elements were also determined with LA-ICP-MS [35].

2. Analytical method

2.1. Instrumental setup

We carried out the REEs analyses with CAMECA NanoSIMS 50L at Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The O^- primary beam can be optimized to a minimum diameter of ~ 0.4 μm with an intensity of 2–4 pA. However, the secondary ions intensity of rare earth elements generated by this small beam is as low as 0.01 count per second (cps), which is at the noise level of the electron multiplier (EM) detectors. In order to obtain sufficient counting statistics and to achieve a detection limit as low as 0.01 ppm, a much higher beam current of ~ 1 nA was used. The O^- primary beam has an impact energy of 16 keV, it was optimized to ~ 2.5 μm in diameter (Fig. 1). The density of primary beam was ~ 21 mA/cm 2 , similar to the situation applied by Yang et al. and higher than other types of SIMS [16]. To stabilize the secondary ion yields [16,36], the primary beam of 1 nA was scanned over an area ranging from 5×5 μm^2 to 10×10 μm^2 on the samples. The build-up of negative charge on the analytical spot was alleviated via secondary electron draining to the Au coat through the edge of the crater [37,38].

To eliminate the isobaric interferences of LREE oxides to HREEs and other interferences of molecular species from the matrix, a high mass resolution of ~ 10000 ($M/\Delta M$ measured at 10% peak height, Fig. 2) and a transmission of $\sim 15\%$ (relative to full transmission without slits and apertures) were achieved, applying entrance slit (10 μm), aperture slit (80 μm) and exit slit (90 μm). In addition, we finely adjusted the focus plane of the multi-collectors the analysis and deflectors to achieve high mass resolution all detectors. REE isotopes of ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{161}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb and ^{175}Lu measured, and $^{30}\text{Si}^+$ or $^{42}\text{Ca}^+$ was counted as the internal reference. All these ions were sequen-

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