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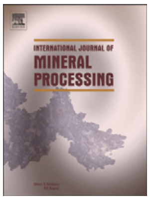

Characteristics of zircon suitable for REE extraction

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ABSTRACT

Zircon ($ZrSiO_4$) from Naegi and Ohro granitic pegmatites, Japan and from Saigon alkali basalt, Vietnam, were mineralogically characterized by inductively couples plasma mass spectrometry (ICP-MS), electron-microprobe analysis (EMPA), X-ray powder diffraction, micro-Raman spectroscopy and leaching experiment. The powder XRD and Raman spectra analyses show that the degree of metamictization increases in the following order: Saigon (crystalline), Ohro (partly metamict) and Naegi zircons (fully metamict). Quantitative analytical results by the EMPA indicate that the Naegi and Ohro zircon samples contain a large amount of REE_2O_3, while REE_2O_3 contents in Saigon zircon are below detection limit. The leaching experiments using a solvent 1 M-HCl for the present zircons under the condition at a room temperature to 250 °C and retention time of 30 h resulted in about 100%, 50% and 1% recoveries of REE from the Naegi, Ohro and Saigon zircons, respectively. Leaching experiments for the Naegi zircon at different temperatures and retention time 30 h, showed that a significant amount of REE was leached out at the temperature above 150 °C, although REE were hard to be leached at a room temperature (about 25 °C). Therefore, both low crystallinity of zircon and higher leaching temperature are requisite for effective leaching of REE from zircon.

1. Introduction

Zircon is the common accessory mineral in the majority of igneous and metamorphic rocks with Zr as an essential structural constituent (Hoskin and Schaltegger, 2003). Zircon, generally being a heavy mineral and being resistant to chemical decomposition and erosion, is concentrated with other heavy resistant minerals in placer deposits, principally in river and beach sands (Abdel-Rehim, 2005). Hoskin and Schaltegger (2003) argued that zircon contains generally less than 1 wt% ΣREE + Y, and attributed to the analyses with significantly higher REE abundances to alteration and/or accidental analysis of inclusions. However, many varieties of zircon containing a large amount of REE, Th, U, Nb and Ta have been reported from granitic pegmatites and the granitic rocks undergoing a metasomatic process such as greisenization and albitization (e.g., Johan and Johan, 2005; Abdalla et al., 2009; Hoshino et al., 2010), and attempts to exploit zircon from granites and peralkaline rocks as a heavy REE source are conducted. Most of the zircons into which REE are extraordinarily incorporated, preferentially incorporate the radioactive elements such as Th and U. Hence such zircons often occur in the metamict state (Hoshino et al., 2010). Leaching of REE from these metamict zircons may be easier owing to low crystallinity. Actually, some previous studies suggested that Pb, and in some cases U, can be removed during aqueous alteration, and that the degree of Pb loss depends on the degree of radiation damage to the zircon structure, the chemical nature of the aqueous solution, temperature, pressure and duration of the experiment (e.g., Sinha et al., 1992; Rizvanova et al., 2000). The objective of the present study is to describe characteristics of zircon suitable for REE leaching through mineralogical and leaching experiments.

2. Experimental

This study used REE-rich zircons from Naegi and Ohro granitic pegmatites in Japan (e.g., Hoshino et al., 2010) and chemically pure zircon from Saigon alkali basalt in Vietnam (Garnier et al., 2005) for leaching experiment. The degree of crystallinity for each zircon was examined by X-ray powder diffraction (PXRD) analysis. Samples were X-rayed with Cu-$K\alpha_1$ radiation (40 kV, 20 mA) using a Rigaku RAD-A system with a flat graphite mono-chromator and 1º divergence slit at University of Tsukuba. Whole patterns from 3 to 60º 2θ were scanned at 0.5°/minute steps. The zircon samples were ground in an agate pestle until their powders became sufficiently small to avoid the problems associated with micro-absorption. Silicon metal powder was used as an angle-calibration internal standard for angle diffraction. Each mixture of zircon sample (1 g) and silicon powder standard (0.1 g) was applied to the no-reflection quartz plate. Similar XRD analyses were carried out for powder sample collected after leaching experiment (powder zircon collected after leaching experiment: 20 mg, silicon powder standard: 0.2 mg). Crystallinity and

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colors of zircon powder were compared before and after the present leaching experiments. The chemical compositions of zircon grains were determined by a JEOL JXA-8900 electron microprobe equipped with five wavelength-dispersive spectroscopes (WDS) at AIST. Chemical zoning of zircon was recorded using BSE images in high resolution. Qualitative analyses were made using 20 kV accelerating potential and 1.0×10^{-7} A beam current. Elements detected with qualitative analyses were quantitatively measured by using an accelerating voltage of 20 kV, a beam current of 2.0×10^{-8} A, count times of 20 s and a beam diameter of 1–2 μm. For chemical analysis of zircon powder, glass bead, or fusion of the sample and flux ($Li_2B_4O_7$) mixture in the proportion of 50 mg : 500 mg, were prepared. The glass beads were finely pulverized in agate mortar and decomposed by mixed acid of HNO_3, HF and $HClO_4$. The chemical compositions of solution obtained from the decomposition of zircon powder were determined by inductively couples plasma mass spectrometry (ICP-MS) in laboratory of Shin-Etsu Chemical Co., Ltd., Japan.

Raman spectra of the zircon samples were measured to assess the degree of radiation damage and to investigate the relative variability in both H_2O content and crystallinity of zircon crystals. Raman scattering measurements were carried out using a micro-Raman spectrometer (HORIBA YVON) with a CCD detector (ANDOR, 255 × 1024 pixcel, -70 °C). Approximately 20 mW at 514.5 nm wavelength from an Ar laser (melles GRIOT 175B-100B) and count times of 10 s were used for excitation. The measurement was made under ambient conditions.

Leaching experiments of zircon powders were performed in 45 ml Teflon-lined Parr acid digestion vessels and heated in Yamato Drying Oven (DX302) for 30 h. After reaction, the vessels were cooled to a room temperature in air. The heating temperature was constant and accurate within 10 °C. Geisler et al. (2003b) reported recrystallization of fully amorphous zircon by the reaction with HCl solution and leaching of Zr and Si from the zircon. Thus for leaching experiments in this study HCl is used as leaching solution. For each experiment about 30 ml HCl solution was added to 30 mg zircon powder. Ten series of hydrothermal leaching experiments were designed to evaluate the influence of their solution temperatures and solution pH on each sample. Leached zircon powder was filtered through filter paper. The chemical compositions of the lleachate were determined by ICP-MS in laboratory of Shin-Etsu Chemical Co., Ltd., Japan. Based on the results, leached ratio of each element was calculated.

Table 1
The d-spacing, full width at half maximum (FWHM) intensity and full intensity for the (200) (112) and (312) reflections of zircons from Naegi, Ohro and Saigon before and after leaching experiments.

Sample	*d* (Å)	FWHM (2θº)	Intensity (counts/mg)
		(200) reflection	
Naegi	n.d.[a]	n.d.	n.d.
Naegi, room temperature, 1 M HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 50 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 100 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 150 C°, 1 M-HCl, 30 h	3.33	0.379	57.0
Naegi, 200 C°, 1 M-HCl, 30 h	3.31	0.326	57.7
Naegi, 250 C°, 1 M-HCl, 30 h	3.32	0.354	78.4
Ohro	3.33	0.505	21.8
Ohro, room temperature, 1MHCl, 30 h	3.33	0.372	51.0
Ohro, 250 C°, 1 M-HCl, 30 h	3.34	0.256	98.4
Ohro, 250 C°, 6 M-HCl, 30 h	3.31	0.166	165
Saigon	3.30	0.125	913
Saigon, 250 C°, 1 M-HCl, 30 h	3.30	0.146	951
		(112) reflection	
Naegi	n.d.**	n.d.	n.d.
Naegi, room temperature, 1MHCl, 30 h	n.d.	n.d.	n.d.
Naegi, 50 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 100 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 150 C°, 1 M-HCl, 30 h	2.54	1.09	5.01
Naegi, 200 C°, 1 M-HCl, 30 h	2.54	0.483	12.8
Naegi, 250 C°, 1 M-HCl, 30 h	2.52	0.517	20.8
Ohro	2.54	0.377	12.2
Ohro, room temperature, 1MHCl, 30 h	2.54	0.400	38.9
Ohro, 250 C°, 1 M-HCl, 30 h	2.53	0.225	84.3
Ohro, 250 C°, 6 M-HCl, 30 h	2.53	0.164	119
Saigon	2.52	0.103	204
Saigon, 250 C°, 1 M-HCl, 30 h	2.52	0.142	155
		(312) reflection	
Naegi	n.d.**	n.d.	n.d.
Naegi, room temperature, 1MHCl, 30 h	n.d.	n.d.	n.d.
Naegi, 50 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 100 C°, 1 M-HCl, 30 h	n.d.	n.d.	n.d.
Naegi, 150 C°, 1 M-HCl, 30 h	1.73	0.549	9.32
Naegi, 200 C°, 1 M-HCl, 30 h	1.72	0.572	13.4
Naegi, 250 C°, 1 M-HCl, 30 h	1.72	0.452	24.9
Ohro	1.73	0.485	7.10
Ohro, room temperature, 1MHCl, 30 h	1.72	0.385	20.8
Ohro, 250 C°, 1 M-HCl, 30 h	1.73	0.355	44.6
Ohro, 250 C°, 6 M-HCl, 30 h	1.72	0.192	93.1
Saigon	1.71	0.151	187
Saigon, 250 C°, 1 M-HCl, 30 h	1.71	0.161	203

3. Results

X-ray powder diffraction lines, (200), (112) and (312), characteristic of zircons from the Naegi, Ohro and Saigon, respectively, are compared in Table 1 and Fig. 1. The metamictization process of zircon has a great influence on both intensities and *d*-spacings of its diffraction lines (e.g., Murakami et al., 1991). With decreasing degree of lattice ordering, diffraction peaks appear to become less intense and less sharp. As is evident from Table 1 and Fig. 1, the XRD peaks of the Ohro zircon are lower in both sharpness and intensity, compared to those of the Saigon zircon. At the same time, the peaks of the Ohro zircon are displaced towards smaller 2θ angle (i.e. larger *d*-spacings). No clear peaks are observed for the Naegi zircon. The change in intensity and sharpness of these peaks reflect the degree of metamictization, which increases in the following order: Saigon, Ohro and Naegi.

In BSE images, the Naegi and Ohro zircons from the granitic pegmatites show a porous texture with Th-U mineral microinclusions such as xenotime, thorite and coffinite, but these minerals were not detected by PXRD, whereas the zircon from Saigon does not contain any inclusion (Fig. 2). Representative chemical analyses of these zircons are listed in Table 2. The quantitative data indicates that zircons from Ohro and Naegi granitic pegmatite are enriched in REE (Naegi: 4.76 wt% REE_2O_3, Ohro: 11.17 wt% REE_2O_3), whereas Saigon zircons is relatively REE- poor (Table 2). Among these zircons, the Ohro zircon yielded the low analytical totals obtained by EMPA (Table 2). The micro-Raman spectroscopy analysis shows a broad band around 3400 cm^{-1} for the Ohro zircon, which represents presence of molecular water in the zircon (Fig. 3). In contract, this broad band around 3400 cm^{-1} was not observed for the zircons from Naegi and Saigon (Fig. 3). This observation suggests that these two zircon samples do not contain molecular water. Nasdala et al. (1995) suggested that all main Raman bands shift toward lower wave numbers, decrease in intensity, and become broader with increasing radiation induced damage. Raman spectra (especially around 1000–1500 cm^{-1}) of the Ohro and Naegi zircons are broader and lower from those of the pure reference zircons from Saigon (Fig. 3). The different intensity and sharpness of the Raman bands of these zircons is consistent with the results of PXRD.

The chemical compositions of zircon powder measured by ICP-MS, which are used for the calculation of REE recovery, are shown in Table 3. The leaching experiments for the zircons using a solvent 1 M-HCl under the condition of heating temperature 250 °C and retention time 30 h, showed that recoveries of REE from the Naegi, Ohro and Saigon zircons are about 100%, 50% and 1%, respectively (Table 4). The leaching experiments for the Naegi zircon using the same solvent under the condition of a solvent 1 M-HCl, room temperature (about 25 °C) and heating temperatures 50 °C, 100 °C, 150 °C and 200 °C and retention time 30 h showed the recoveries of REE