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Research paper

In situ U–Pb and Nd–Hf–(Sr) isotopic investigations of zirconolite and calzirtite

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ABSTRACT

Although the calcium- and titanium-bearing zirconsilicates, zirconolite and calzirtite, are common minerals in carbonatites little is known regarding their trace element or isotopic characteristics. Available data indicate that they can have significant contents of U, Pb, Nb, Ta, Zr, Hf, rare earth elements (REEs), minor Sr and low Rb/Sr and Lu/Hf ratios. Their compositions indicate that they have potential for U–Pb age determination together with Nd–Hf and possibly Sr isotopic analyses. In this study, zirconolite and calzirtite from carbonatites occurring at Phalaborwa (South Africa), Prairie Lake (Canada), Afrikanda and Kovdor (Kola, Russia), Guli (Siberia, Russia) and Jacupiranga (Brazil) were selected for an isotopic analysis by *in situ* techniques. Ion microprobe analyses using a CAMECA 1280 ion microprobe show that reliable Pb–Pb ages can be obtained from these minerals as they have extremely high U concentrations, coupled with negligible common Pb. Although these minerals have low Rb/Sr ratios, their low Sr concentrations, in most cases, render *in situ* Sr isotopic analyses difficult. In contrast, their high Sm, Nd and Hf concentrations, with generally low Lu/Hf ratios, permit precise *in situ* isotopic analysis of Nd and Hf.

1. Introduction

Zirconium-bearing minerals are widely distributed in a variety of igneous and metamorphic rock types. Of these, zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), are very important minerals for U–Pb geochronology, Hf and O isotopic analyses (Davis et al., 2003; Kinny and Maas, 2003; Valley, 2003). Their compositions provide information used to constrain the temperatures of magmas and their source characteristics (Hoskin and Schaltegger, 2003; Hanchar and Watson, 2003). Although some investigations have been conducted, it is generally accepted that zircon and baddeleyite are not suitable for Sr and Nd isotopic analyses (Kinny and Maas, 2003; Amelin, 2004), limiting our ability to discuss petrogenesis given that coupled Sr–Nd isotopic data are also vital for this purpose.

Other relatively common zirconium-bearing minerals include: eudialyte; catapleiite; gittinsite; sabinaite; weloganite; tazheranite; zirconolite/zirkelite; kimzeyite; wadeite; and calzirtite. Eudialyte occurs principally in peralkaline nepheline syenite, whereas catapleiite, gittinsite, sabinaite, weloganite and many other zirconium-bearing silicates, e.g., dalyite, occur in a variety of alkaline rocks including peralkaline granites. Some are of subsolidus metasomatic/hydrothermal origin and result from the breakdown of magmatic minerals such as eudialyte.

Zirconolite ($CaZrTi_2O_7$) is an accessory mineral in carbonatites, mafic–ultramafic rocks and syenites (Williams and Gieré, 1996, and reference therein). Although it is known that zirconolite contains significant concentrations of U, there have been few investigations of its suitability for U–Pb geochronology. Commonly, the mineral is difficult to recognize and is usually too small to be separated for isotopic dilution analyses by thermal ionization mass spectrometry (TIMS) (Hinthorne et al., 1979; Oversby and Ringwood, 1981; Heaman and LeCheminant, 1993). Only recently, has it been shown that zirconolite can be used for *in situ* age determinations using sensitive high-resolution ion microprobe (SHRIMP, Rasmussen and Fletcher, 2004; Rasmussen et al., 2008, 2009), and nano secondary ion mass spectrometry (NanoSIMS) techniques with reliable age precision (Stern et al., 2005). Although it has long been recognized that zirconolite contains high Sr, Hf and rare earth elements (REEs) (Harding et al., 1982; Mazzi and Munno, 1983; Purtscheller and Tessadri, 1985; Fowler and Williams, 1986; Platt et al., 1987; Williams, 1996; Williams and Gieré, 1996; Gieré et al., 1998; Bellatreccia et al., 1999, 2002; Della Ventura et al., 2000, 2001; Dawson et al., 2001; Carlier and Lorand, 2003, 2008; Zaccarini et al., 2004; Rajesh et al., 2006; Rasmussen et al., 2008; Azzone et al., 2009), there are no published studies of its Sr, Nd and Hf isotopic compositions.

Zirkelite [$(Ca,Th,Ce)Zr(Ti,Nb)_2O_7$] is cubic and is a pyrochlore-group mineral (White, 1984; Bayliss et al., 1989), which is compositionally

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similar to zirconolite (Harding et al., 1982; Bulakh et al., 1998). There have been few previous attempts to use this mineral for U–Pb age determinations or Sr–Nd–Hf isotopic analysis (Busche et al., 1972). Calzirtite ($Ca_2Zr_5Ti_2O_{16}$) is a common mineral in carbonatite and associated pyroxenite and phoscorite (van der Veen, 1965; Bulakh et al., 1967, 1998; Williams and Gieré, 1996). In common with zirkelite, U–Pb age determinations have not been undertaken on this mineral. Limited compositional data indicate that calzirtite might contain less REE than zirconolite or zirkelite (Bellatreccia et al., 1999).

In this study, zirconolite and calzirtite from numerous localities were selected for U–Pb isotopic age determination using the CAMECA1280 SIMS. Sr–Nd–Hf isotopic analysis was undertaken using a Neptune multi-collector (MC) inductively-coupled plasma mass spectrometry (ICM-MS) instrument. Our objective is to develop a technique to obtain coupled Pb–Pb age and Sr–Nd–Hf isotopic data which are of use with regard to the petrogenesis of the magma from which zirconolite and calzirtite crystallized.

2. Analytical methods

Separated mineral grains of zirconolite and calzirtite from several localities (see below) were handpicked, mounted in epoxy resin, and polished until the grain centers of the grains were exposed. Before isotopic analysis, back-scattered electron (BSE) images were obtained using a JEOL JXA8100 electron microprobe, in order to assess internal compositional variation and textures, and identify potential target sites for Pb–Pb and Sr–Nd–Hf analyses. All analyses were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Cubic zirkelite is compositionally similar to monoclinic zirconolite, and thus difficult to distinguish from the latter on the basis of composition alone. Therefore, as suggested by Bayliss et al. (1989), we use the general name of zirconolite to refer to all material with a “zirconolite” overall composition.

2.1. Major and trace element analyses

Major element compositions were obtained using a JEOL–JAX8100 electron microprobe with a 15 kV accelerating potential and 12 nA beam current. Counting times were 20 s. Total iron is expressed as FeO. The analytical uncertainties are within 2% for TiO_2 and CaO, but ~10–20% for other elements due to their low concentrations. Prior to analysis, BSE images were obtained to identify analysis spots.

Trace element compositions (including REE) were conducted using an Agilent 7500a quadruple laser ablation inductively-coupled plasma mass spectrometry (Q-ICP–MS), which is equipped with a 193 nm excimer ArF laser ablation system (GeoLas Plus). Helium gas was flushed to minimize aerosol deposition around the ablation site, and mixed with argon gas downstream of the ablation cell. During analyses, a spot size of 30 μm was applied with a repetition rate of 6 Hz. Every five sample analyses were followed by one NIST SRM 610 measurement. Each spot analysis consisted approximately of 30 s of background acquisition and 60 s of sample data acquisition. Trace element concentrations were calculated using GLITTER 4.0 and calibrated using ^{40}Ca as an internal standard and NIST610 as an external reference material (Jackson et al., 2004; Griffin et al., 2008).

2.2. In situ SIMS Pb–Pb analyses

The Pb–Pb analyses of this study were performed using the CAMECA1280 ion microprobe installed at the Institute of Geology and Geophysics in Beijing. The instrument description and analytical procedure can be found in Li et al. (2009), and only a brief summary is given here. The O_2^- primary ion beam was accelerated at 13 kV, with an intensity between 10 and 18 nA. The analysed ellipsoidal spot size is about 20 × 30 μm in size. Positive secondary ions were extracted with a 10 kV potential.

All samples analysed in this study were cast in epoxy mounts. Each mount was coated with about 30 nm of high-purity gold to reach <20 Ω resistance. The multi-collector mode equipped with four ion-counting electron multipliers was used to measure secondary ion beam intensities of ^{204}Pb, ^{206}Pb, ^{207}Pb and an matrix reference peak of $^{40}Ca^{48}Ti_2^{16}O_4^+$ at a mass resolution of ~8000 (at 50% peak height, fixed exit slit). The ^{206}Pb signal was used as reference peak for tuning the secondary ions. A Nuclear Magnetic Resonance (NMR) controller was used in multi-collector measurements; this stabilized the magnetic field with an instrumental drift (ΔM/M) less than 2 ppm over 20 min. For Pb isotopes analyses, each measurement consists of 70 cycles, with the total analytical time being about 12 min.

The relative efficiencies of the secondary ions of the electron multipliers (EM) on the movable trolleys relative to the axial EM were calibrated by measurement of the NIST 610 standard with well-defined Pb isotopic compositions as determined by TIMS. All other effects that may affect the Pb isotope measurement, including instrumental mass fractionation of Pb isotopes, Pb hydrides and drift of EMs efficiencies, were monitored by analyses of a Phalaborwa baddeleyite standard that was alternately measured with every three unknowns. Difference between the measured $^{207}Pb/^{206}Pb$ ratios of the Phalaborwa baddeleyite and the recommended value of 0.12718 (Heaman, 2009) were applied to an external correction of $^{207}Pb/^{206}Pb$ ratios of unknowns. The daily variation of the measured $^{207}Pb/^{206}Pb$ ratio of the Phalaborwa baddeleyite is usually within 0.2% (1 RSD). The $^{207}Pb/^{206}Pb$ weighted ages with 2σ or 95% confidence level were calculated using ISOPLOT 3.0 (Ludwig, 2003).

2.3. In situ Sr–Nd–Hf isotopic analyses by laser ablation

The *in situ* Sr–Nd–Hf isotopic analyses were conducted using the Neptune MC–ICP–MS instrument. Detailed analytical protocols were given by Xie et al. (2008), Yang et al. (2008, 2009) and Wu et al. (2006), only brief summary is given here.

The Sr isotopic data were acquired in static, multi-collector mode with low resolution using eight Faraday collectors, and the mass configuration array from ^{83}Kr to ^{88}Sr, monitoring Kr and Rb (Yang et al., 2009). Prior to analysis, collectors were aligned using a tuning solution which contains Rb, Sr, Er, and Yb. An aliquot of 200 ppb NIST 987 standard was used regularly for controlling the quality and optimizing the operation parameters, including the torch position, the Ar flow rate, and the ion lens focus, to obtain maximum sensitivity. During the data reduction process, the effects of interfering elements were accounted for in the order Kr, Yb^{2+}, Er^{2+} and Rb, but interferences from Fe dioxides, and Ga and Zn oxides, are not considered due to their low signals during actual analyses. Similarly, no corrections for $^{176}Lu^{2+}$ and $^{176}Hf^{2+}$ on ^{88}Sr were considered as their interferences on ^{88}Sr are negligible. Prior to every analytical session, the Neptune MC–ICP–MS was always configured to monitor Kr in the Ar gas after optimization, especially when a new liquid Ar tank was installed. During analyses, a 50 second measurement of the gas blank was carried out before ablation in order to correct for Kr. On the basis of the method proposed by Ramos et al. (2004), we monitored the presence of $^{167}Er^{2+}$, $^{171}Yb^{2+}$ and $^{173}Yb^{2+}$ at masses 83.5, 85.5 and 86.5. Then the contributions of $^{168}Er^{2+}$ and $^{168}Yb^{2+}$ to ^{84}Sr, $^{170}Er^{2+}$ and $^{170}Yb^{2+}$ to ^{85}Sr (+^{85}Rb), $^{172}Yb^{2+}$ to ^{86}Sr, $^{174}Yb^{2+}$ to ^{87}Sr (+^{87}Rb), and $^{176}Yb^{2+}$ to ^{88}Sr were calculated according to the isotopic abundances of Er and Yb (Chartier et al., 1999; Vervoort et al., 2004). The natural ratio of $^{85}Rb/^{87}Rb$ (2.5926) was used for isobaric correction of Rb by the exponential law, assuming that rubidium has the same mass discrimination as strontium (Ehrlich et al., 2001). In order to avoid the potential matrix-matched effect, an in-house zirconolite standard (Phala-ZrkA) was used for external correction.

The laser ablation Nd isotope technique is similar to that for Sr isotope analysis as described above. Before analysis, a standard Nd solution was used to calibrate the machine and the exponential law