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Evaluating baddeleyite oxygen isotope analysis by secondary ion mass spectrometry (SIMS)

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ABSTRACT

Two baddeleyite megacrysts were evaluated as potential reference materials (RMs) for SIMS oxygen isotope analysis, and utilized to understand and calibrate instrumental mass fractionation (IMF). A baddeleyite crystal (S0045) from the Phalaborwa carbonatite, South Africa has a mean $\delta^{18}O_{VSMOW} = +4.6 \pm 0.3‰$ (range 0.75‰) measured using laser fluorination gas source mass spectrometry (LF-GMS) and one (S0069) from the Mogok metamorphic belt, Myanmar has $\delta^{18}O_{VSMOW} = +22.2 \pm 0.4‰$ (range 0.89‰). SIMS standardization utilizing these inherently heterogeneous RMs is possible by analyzing a number of crystal fragments and utilizing one of them lying at the median of the range. Metamictization, lattice orientation, and chemical composition do not appear to be significant (< 0.5‰) variables in matrix matching of RMs and unknowns. Propagation of errors while utilizing the imperfect RMs results in 10 μm diameter spot uncertainties of about ± 0.3‰ (2σ).

SIMS oxygen isotope analysis of co-crystalline zircon and baddeleyite from the 2.2 Ga Duck Lake sill (DLS) in the Northwest Territories, Canada, yield predominant $\delta^{18}O_{VSMOW}$ modes of +6.0‰ and +3.2‰, respectively. This difference is consistent with preserving high-temperature isotopic equilibrium between zircon and baddeleyite. DLS baddeleyite $\delta^{18}O$ data as a whole are negatively skewed (to 0.0‰), and interpreted to reflect low temperature, open-system behaviour. Zircon $\delta^{18}O$ are less affected, but also show hints of the same influences of secondary alteration and oxygen isotope exchange.

1. Introduction

Baddeleyite (ZrO_2) is a trace phase occurring in ultramafic, mafic, andesitic, trachyte-trachyphonolitic, monzonitic, kimberlitic and carbonatitic igneous rocks, it is produced during metamorphism in some skarns and metacarbonates, and is found in some tektites and meteorites (Heaman and LeCheminant, 1993; Stockstill et al., 2002; Heaman, 2009; Niihara, 2011; Moser et al., 2013; Wu et al., 2015; Li et al., 2016). Baddeleyite preferentially incorporates U (up to 5000 ppm) into its structure during crystallization, and excludes Pb, making it an excellent mineral for U-Pb geochronology. The use of the U-Pb baddeleyite geochronometer to date mafic rocks, especially Precambrian diabase dykes, has increased rapidly in recent years, facilitated by improved extraction techniques designed to recover micro-baddeleyite (< 100 μm) crystals (e.g., Söderlund and Johansson, 2002), and in-situ dating techniques by secondary ion mass spectrometry (Wingate and Compston, 2000; Chamberlain et al., 2010; Li et al., 2010). As baddeleyite is now commonly used to date mafic rocks, other aspects of its geochemistry have been utilized to provide information on the origin and evolution of these rocks, such as trace elements (Reischmann et al., 1995; Rodionov et al., 2012) and hafnium isotopes (Schärer et al., 1997; Xie et al., 2008; Ibanez-Mejia et al., 2014; D'Abzac et al., 2017).

The oxygen isotopic composition of baddeleyite has so far received relatively little attention despite its potential for providing important information on the origin and contamination history of mafic/ultramafic magmas and post-emplacement hydrothermal alteration. For zircon, it is now understood that Pb loss and oxygen isotope disturbance is often associated with hydrothermal alteration (Bibikova et al., 1982; Valley et al., 1994; Valley, 2003; Booth et al., 2005; Davies et al., 2015). Similarly, the oxygen isotopic composition of baddeleyite could

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potentially be used to help understand the cause(s) of baddeleyite U-Pb discordance. Although baddeleyite is typically less discordant than co-existing zircon in a sample (e.g. Heaman and LeCheminant, 2000; Amelin and Zaitsev, 2002; Davies and Heaman, 2014; Schaltegger and Davies, 2017), there is a growing number of examples of baddeleyite discordance (e.g., Corfu et al., 2013; Almeida et al., 2017), and possibly this characteristic is accentuated by sampling bias.

Only two studies have previously investigated the oxygen isotopic composition of baddeleyite. Valley (2003) reported a $\delta^{18}O$ value of $+3.5 \pm 1.5$‰ for 6 fragments of megacrystic baddeleyite from the Phalaborwa carbonatite analyzed by laser fluorination isotope ratio mass spectrometery (LF-GMS), and Wotzlaw et al. (2012) analyzed baddeleyite combined with garnet from the Skaergaard intrusion by LF-GMS and reported a $\delta^{18}O$ of $+2.04 \pm 1.12$‰.

As for U-Pb analysis, the high spatial resolution of SIMS is ideal for baddeleyite oxygen isotopic analysis, since baddeleyite crystals in mafic rocks are typically very small and platy, e.g. < 100 μm along the c-axis and < 20 μm thick (e.g., Chamberlain et al., 2010). However, SIMS analytical protocols and reference materials for oxygen isotope analysis of baddeleyite are lacking. In considering the potential complications of analyzing baddeleyite O-isotopes by SIMS, orientation-related matrix effects on instrumental mass fractionation (IMF) will clearly be important to investigate, as these have been well-documented in analyzing U-Pb isotopes in baddeleyite (Wingate and Compston, 2000; Chamberlain et al., 2010; Schmitt et al., 2010). Crystal-orientation-related matrix effects have also been found in analysis of O-isotopes in other oxides including hematite, magnetite and rutile (Lyon et al., 1998; Taylor et al., 2012; Huberty et al., 2010; Shulaker et al., 2015). Consideration must also be given to isotopic fractionation correlated with other matrix variables, such as metamictization (e.g., White and Ireland, 2012) and crystal chemistry (e.g., Eiler et al., 1997; Vielzeuf et al., 2005; Ickert and Stern, 2013).

Here we explore for the first time the potential for measuring O-isotopes by SIMS using two natural baddeleyite megacrysts, which were selected for practical reasons, as most igneous rocks contain crystals that are too rare and too small for testing both with SIMS and LF-GMS. To supplement our study on baddeleyite megacrysts, we also investigated the oxygen isotope composition of co-existing zircon and baddeleyite to help evaluate the SIMS baddeleyite oxygen isotope methodology and to provide insight into the relationship between U-Pb systematics and oxygen isotopes in baddeleyite.

2. Sample descriptions

We selected one baddeleyite megacryst (~2 cm in diameter) from the Phalaborwa carbonatite complex South Africa and another from the Mogok metamorphic belt Myanmar. The 2060 Ma Phalaborwa carbonatite contains plentiful mm- to cm- sized baddeleyite phenocrysts that are used as reference materials in U-Pb geochronology (see Heaman, 2009). The crystal used in this study was selected based on its euhedral morphology and lack of visible alteration and inclusions. The selected crystal (given Canadian Centre for Isotopic Microanalysis (CCIM) sample number S0045) was broken into fragments 50–250 μm in length for SIMS and LF-GMS analysis.

The Cenozoic Mogok metamorphic belt in Myanmar contains marbles and associated placer deposits of corundum, spinel, and forsterite, with accessory zircon and baddeleyite (Searle et al., 2007; Garnier et al., 2008). The Mogok baddeleyite crystal used in this study was obtained commercially. The 2 cm-long euhedral crystal (CCIM sample number S0069) was selected for analysis based on its pristine appearance and was broken into 50–250 μm fragments. The $\delta^{18}O$ compositions of metamorphic calcite, dolomite and zircon from the Mogok metamorphic belt have been previously reported by Garnier et al. (2008) and Cavosie et al. (2011), both yielding strongly positive values ($\delta^{18}O_{VSMOW} = +19.9$ to $+27.8$‰ in carbonates and $+18$ to $+25.5$‰ in zircon) suggesting that they originated from metamorphism of marine carbonates.

It should be pointed out that the initial fragmentation of these crystals is, in fact, a procedure to be avoided in evaluating megacryst homogeneity, as any overall systematic variations are lost. Preliminary evaluation in section should precede fragmentation.

Large (> 1 cm) baddeleyite crystals are unusual in the geological record, so to test the technique on more typical baddeleyite samples we also examined ~30–70 μm long bladed baddeleyite crystals from the Duck Lake sill (DLS, Bleeker and Kamo, 2003; Bleeker et al., 2007), a Paleoproterozoic mafic intrusion near Yellowknife, North West Territories, Canada. The DLS is un-metamorphosed and both the baddeleyite and zircon crystals have been dated by U-Pb isotope dilution thermal ionization mass spectrometry (ID-TIMS). Both minerals give indistinguishable, near concordant ages of 2181 ± 2 Ma ($^{207}Pb/^{206}Pb$ weighted mean age, Bleeker and Kamo, 2003). The baddeleyite and zircon grains used in this study (CCIM samples number S0218 and S0219, respectively) were provided by Dr. Sandra Kamo at the University of Toronto and are part of the same sample used for U-Pb dating.

Also, chemically pure synthetic monoclinic ZrO_2 (baddeleyite) crystals (2–5 mm in size) were obtained commercially from Zicar Zirconia, Inc. These crystals were used to compare crystal structures between the natural baddeleyite RMs, and the synthetic baddeleyite, as it should have a perfectly crystalline monoclinic structure. Although not reported here, we found this particular source of material to be far too heterogeneous in CL response and in SIMS oxygen isotopes for further consideration as a reference material, but further evaluation of synthetic material is warranted.

3. Analytical techniques

3.1. Laser fluorination-isotopic ratio mass spectrometry

LF-GMS analyses were conducted at the University of Oregon and also the University of Lausanne following the techniques described in Bindeman et al. (2008) and Lacroix and Venneman (2015), respectively. All samples were pretreated with a gas of BrF_5 to reduce blank contributions before being heated by a 35 W CO_2 laser. The extracted gas was purified by a series of cryogenic traps cooled with liquid nitrogen and a mercury diffusion pump. The oxygen gas from each sample was converted to CO_2 using graphite and the CO_2 was measured on a MAT 253 mass spectrometer. For the Oregon analyses, replicates of the in house standard Gore Mountain garnet UOG ($\delta^{18}O_{VSMOW} = +6.52$) were utilized for quality control and bias correction. For the measurements in Lausanne, six measurements of two internal standards were used, 2 of NBS-28 and four of an in house standard LS-1 Qtz. Both standards were identical to the accepted values, with the LS-1 Qtz producing a value of $+18.05 \pm 0.16$‰ and the NBS-28 producing a value of $+9.65 \pm 0.06$‰ (the accepted values are $+18.1$‰ and $+9.64$‰ respectively).

3.2. Secondary ion mass spectrometry (SIMS)

All SIMS measurements were conducted at the Canadian Centre for Isotopic Microanalysis (CCIM) at the University of Alberta using a Cameca IMS1280 multi-collector ion microprobe. The experiments were conducted on 7 grain mounts in 9 ion probe sessions over a three year period. Each mount contained at least 40 fragments of Phalaborwa S0045 and Mogok S0069 baddeleyite along with Temora 2 and Mud Tank zircons for instrument set up. Duck Lake zircon and baddeleyite crystals were also included on one mount. Epoxy grain mounts were prepared using West System® 105 and 206 resin and hardener, respectively. Mechanical grinding and final polishing utilized 9, 3, and 1 μm diamond compounds and resulted in flat mounts with no topography. After polishing, the mounts were cleaned ultrasonically with a soap solution and deionized H_2O, and dried in an oven at 50 °C. Mounts were sputter-coated with 5 nm of Au prior to scanning electron

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