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Small-volume baddeleyite (ZrO_2) U–Pb geochronology and Lu–Hf isotope geochemistry by LA-ICP-MS. Techniques and applications

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ABSTRACT

U–Pb geochronology of baddeleyite (ZrO_2) is an increasingly used tool in the Earth and planetary sciences for determining the crystallization and emplacement ages of mafic igneous rocks. Additionally, baddeleyite has a strong affinity for hafnium and preferentially excludes the REE's, making it an important repository of Hf isotopic compositions, which can be used to provide constraints on the origin of these rocks. In this contribution we introduce a technique for U–Pb dating and Lu–Hf isotopic analysis of baddeleyite by LA-MC-ICP-MS. A systematic study of crystals with known ages demonstrates that our methodology is capable of producing $^{207}Pb/^{206}Pb$ results that are precise and accurate to within 1% of their TIMS values at a 2-sigma confidence level, while Phanerozoic crystals can generally be dated to within 1.5 to 3.0% accuracy using their $^{206}Pb/^{238}U$ compositions. These results are routinely reproducible with a variety of laser-spot sizes ranging from 30 to 10 μm in diameter and with crater depths as shallow as ~3 μm in depth. This represents a significant improvement in the sampled volume generally used for LA-ICP-MS geochronology and is a critical step for dating small baddeleyite crystals either as mineral separates or identified in situ within thin sections. No orientation-dependent biases on the measured $^{206}Pb/^{238}U$ values were identified from our data, suggesting that LA-ICP-MS dating of Phanerozoic crystals can be routinely performed without the biases previously reported for SIMS instruments. Our data show that initial $^{176}Hf/^{177}Hf$ ratios can be determined with an accuracy as good as 0.5 εHf units by taking the mean of 10 to 30 individual spot analyses acquired with a 40 μm beam-diameter. These U–Pb and Hf results are comparable to what can be routinely achieved for zircon by LA-MC-ICP-MS. In addition to the methodological approach, we report a high-precision U–Pb TIMS age and four solution-MC-ICP-MS Hf isotopic results for new and/or important baddeleyite localities. These new data are used here to assess the adequacy of our fractionation, interference and mass-bias corrections and can be used as a basis for addressing the accuracy of LA-ICP-MS U–Pb and Lu–Hf data for future inter-laboratory calibration efforts.

1. Introduction

Baddeleyite is a monoclinic zirconium oxide mineral that commonly occurs as an accessory phase in silica-undersaturated igneous rocks of terrestrial and extraterrestrial origin (Heaman and Lecheminant, 1993; Heaman, 2009; Niihara, 2011; Moser et al., 2013). In recent years it has received increased attention from both geochronologists and petrologists because it can provide essential age and isotopic information about mafic rocks, a lithologic group where the more widely used mineral in geochronology, zircon ($ZrSiO_4$), is often not present (Scoates and Chamberlain, 1995; Chamberlain et al., 2010). Experimental determinations of trace-element partitioning between baddeleyite and carbonatitic melts performed by Klemme and Meyer (2003) have shown that U is over an order of magnitude more compatible in its crystal structure than Pb, and as a result baddeleyite commonly displays Pb isotopic compositions that are dominantly radiogenic. The importance of baddeleyite as a robust U–Pb geochronometer is supported by decades of work on this mineral prompted by the seminal contribution of Krogh et al. (1987), and is reflected in the publication of a recent special volume on Lithos (vol. 174, 2013) highlighting baddeleyite. In addition to its application of obtaining crystallization ages, the strong compatibility of Hf coupled with low REE contents makes it an ideal mineral for obtaining precise Hf isotopic ratios and fingerprinting initial $^{176}Hf/^{177}Hf$ compositions (Patchett et al., 1981). These geochemical aspects make baddeleyite an important tool for the study of mafic rocks on Earth through time.

For over three decades, and despite the explosion of routine U–Pb geochronology brought about by low-blank thermal ionization mass spectrometry (TIMS) and more recently by secondary ion mass spectrometry (SIMS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) methods, the use of baddeleyite as a

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geochronometer has remained relatively under-represented in the geological literature. Several challenges have made baddeleyite geochronology less straightforward than its felsic counterpart, zircon. First, the generally small size of igneous baddeleyite crystals has made its extraction from rock samples a challenging task. Recent improvements in mineral separation techniques, like those presented by Söderlund and Johansson (2002), have helped to overcome this difficulty. Secondly, a major practical limitation to baddeleyite dating by small-volume in-situ techniques is the orientation-dependent Pb/U fractionation reported by previous workers using secondary-ion mass spectrometers (SHRIMP, Wingate and Compston, 2000; CAMECA-IMS1270, Schmitt et al., 2010). This complexity has imposed practical limits on the accuracy and precision to which young baddeleyites can be dated using their $^{206}Pb/^{238}U$ composition, and for older samples it presents issues for evaluating complexities in U–Pb systematics because the real magnitude of discordance can be largely obscured by unaccounted instrumental fractionations. Recent efforts made by Li et al. (2010) and Schmitt et al. (2010) have shown that this effect in SIMS can be minimized by the use of oxygen-flooding techniques and they report a reduction in the scatter of measured $^{206}Pb/^{238}U$ values down to ~2%. These orientation-dependent instrumental biases or "orientation effects" have also been reported for minerals such as rutile (Taylor et al., 2012), magnetite (Kita et al., 2010; Kozdon et al., 2010), and sphalerite (Kozdon et al., 2010). Examples of this phenomenon however, are exclusive to studies using ion-probe instruments and, to our knowledge, have not been observed for any phase or isotopic system during LA-ICP-MS analyses. If the hypothesized physical mechanism responsible for this crystal-orientation effect — the channeling of primary ions along low-index directions in the crystal lattice (Valley and Kita, 2009) — is the source of the measured $^{206}Pb/^{238}U$ scatter in baddeleyites, then this effect would likely not be observed during laser ablation analyses due to its fundamentally different and strongly energetic sampling mechanism (Horn, 2008). However, as a proof of concept and in order to account for the possible existence of any orientation-effects in LA-ICP-MS analyses, we conducted a simple but systematic experiment designed to test its potential effect.

A commonly observed feature in mafic rocks with complex time-temperature histories is that, upon metamorphism, baddeleyite can easily be recrystallized to poly-crystalline zircon aggregates under a wide range of P–T conditions (Davidson and van Breemen, 1988; Heaman and Lecheminant, 1993; Söderlund et al., 2008). At first glance this could be perceived as an apparent disadvantage, but if the right analytic approach is taken then age information can be retrieved for both events responsible for crystal-growth and recrystallization. Different techniques have been successfully employed to isolate these two components, by dating the baddeleyite cores to determine protolith crystallization ages and by dating the zircon rims to determine the timing of metamorphism These approaches have, thus far, mostly employed ID-TIMS techniques with separation of the phases achieved either by mechanical abrasion (e.g., Davidson and van Breemen, 1988) or selective chemical dissolution (e.g. Rioux et al., 2010). In a more recent study, Beckman et al. (2014) used a combination of TIMS and SIMS analyses of remnant baddeleyite cores enclosed in zircon overgrowths in order to obtain protolith ages from metamorphosed gabbros of the Norwegian Caledonides.

Despite the lack of experimental diffusion data for U or Pb in baddeleyite, the retention of concordant or only slightly discordant U–Pb ages from baddeleyite cores that have undergone granulite-grade metamorphism indicates a high closure temperature for the U–Pb baddeleyite geochronometer (Davidson and van Breemen, 1988; Söderlund et al., 2008; Beckman et al., 2014). Nevertheless, it is well known that the diffusive behavior of any element in a particular mineral phase can be strongly influenced by the structural integrity of the crystal lattice, and therefore radiation-induced damage at the time of reheating may play an important role in the degree of discordance (i.e., age resetting) that a mineral system will attain (Cherniak et al., 1991; Mezger and Krogstad, 1997; Cherniak and Watson, 2000; Geisler et al. 2002). In contrast to zircon, where increased radiation dosage through time leads to amorphisation of the crystalline structure (Murakami et al., 1991), it has been shown that monoclinic zirconia is highly resilient to elevated degrees of radiation dosage and undergoes phase transitions to higher-symmetry polymorphs before experiencing metamictization (Sickafus et al., 1999; Simeone et al., 2002, 2006; Valdez et al., 2008). This process, although not yet fully understood or even observed for natural baddeleyites, may have profound implications for the U–Pb systematics of this mineral because localized phase transformations can lead to the development of diffusion sub-domains and create 'fast-paths' through which Pb could become mobile via grain-boundary diffusion.

The development and improvement of techniques capable of producing texturally-resolved analyses in baddeleyites will not only have an impact on its routine application to dating mafic rocks but will also improve our understanding of its U–Pb systematics in ways that are inaccessible to single- or multiple-crystal-dissolution dating methods. In this contribution, we present an analytical method that allows for the rapid, accurate and spatially resolved dating of baddeleyite using LA-MC-ICP-MS, as well as for investigating their Hf isotopic compositions. We also introduce high-precision ID-TIMS and U–Pb and solution-MC-ICP-MS Hf results for new reference crystals and highlight some of the challenges involved in the accurate and precise estimation of baddeleyite U–Pb crystallization ages. These results are a contribution to the PlasmAge LA-ICP-MS network (www.plasmage.org) and EARTHTIME initiative (www.earth-time.org), and could be used for future inter-laboratory comparison and calibration efforts on baddeleyite geochronology (e.g., Bowring et al., 2013 and Kosler et al., 2013 for zircon).

2. Analytical approach, instrumentation and methods

For this study we used baddeleyite crystals with a wide range of ages that formed in a variety of tectonic settings and host-rock compositions. From oldest to youngest, we present results from the Phalaborwa carbonatite massif of South Africa (2059 Ma, Heaman, 2009; Rioux et al., 2010; Wu et al., 2011), the Tomashgorod dolerite of the Ukrainian Shield (1791 Ma, Bogdanova et al., 2013), the Mackmyra, Sorkka and Ämmänpelto dolerites of Fennoscandia in SE Sweden and SW Finland (1258 to 1256 Ma, Suominen, 1991; Soderlund et al., 2004; 2006), the Duluth Complex FC-1 anorthositic gabbro of Minnesota (1099 Ma, Paces and Miller, 1993), the Gällsjön dyke from the Blekinge–Dalarna swarm in eastern Sweden (956 Ma, Ulf Söderlund, personal communication), the Ogden gabbro from the South Carolina Appalachians (412 Ma, this study), the Kovdor carbonatite massif of the Kola Peninsula in Russia (378 Ma, Amelin and Zaitsev, 2002; Rodionov et al., 2012; Schmitt et al., 2010), and the Yinmawanshan gabbro of the Liaodong Peninsula in China (32 Ma, Li et al., 2010; Yuan et al., 2004; Wu et al., 2006). Most of these baddeleyites have previously been dated by ID-TIMS so they provide a good benchmark for assessing the accuracy and reproducibility of our analytical protocol, while also covering a wide range of geologic time; the only exception is the Yinmawanshan gabbro whose age was estimated by baddeleyite SIMS and zircon LA-ICP-MS methods. Most of them, however, had not been previously studied for their Hf isotopic compositions. In order to address the accuracy and reproducibility of our laser-ablation Lu–Hf results, four key samples were also analyzed by solution-MC-ICP-MS to obtain precise $^{176}Hf/^{177}Hf$ reference ratios.

2.1. LA-MC-ICP-MS uranium–lead geochronology

U–Pb isotopic analyses conducted by LA-MC-ICP-MS were all performed at the Arizona Laserchron Center (ALC) at the University of Arizona (www.laserchron.org). The ALC houses a Photon Machines Analyte-G2 ArF Excimer laser-ablation system using a small-volume,