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Do Hf isotopes in magmatic zircons represent those of their host rocks?

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ABSTRACT

Lu–Hf isotopic system in zircon is a powerful and widely used geochemical tracer in studying petrogenesis of magmatic rocks and crustal evolution, assuming that zircon Hf isotopes can represent initial Hf isotopes of their parental whole rock. However, this assumption may not always be valid. Disequilibrium partial melting of continental crust would preferentially melt out non-zircon minerals with high time-integrated Lu/Hf ratios and generate partial melts with Hf isotope compositions that are more radiogenic than those of its magma source. Dissolution experiments (with hotplate, bomb and sintering procedures) of zircon-bearing samples demonstrate this disequilibrium effect where partial dissolution yielded variable and more radiogenic Hf isotope compositions than fully dissolved samples. A case study from the Neoproterozoic Jiuling batholith in southern China shows that about half of the investigated samples show decoupled Hf isotopes between zircons and the bulk rocks. This decoupling could reflect complex and prolonged magmatic processes, such as crustal assimilation, magma mixing, and disequilibrium melting, which are consistent with the wide temperature spectrum from ~630 °C to ~900 °C by Ti-in-zircon thermometer. We suggest that magmatic zircons may only record the Hf isotopic composition of their surrounding melt during crystallization and it is uncertain whether their Hf isotopic compositions can represent the primary Hf isotopic compositions of the bulk magmas. In this regard, using zircon Hf isotopic compositions to trace crustal evolution may be biased since most of these could be originally from disequilibrium partial melts.

1. Introduction

Lu–Hf isotopic system has been widely used as a petrogenetic tracer, yielding information on time-integrated fractionation of Lu and Hf during processes of melting, crystallization, metasomatism, and assimilation (e.g., Patchett, 1983; Blichert-Toft and Puchtel, 2010; Vervoort, 2015). Lu–Hf isotopic system provides a powerful complement to the widely used Sm–Nd isotopic system, owing to similar but greater parent-daughter elemental fractionation during magmatic processes. However, due to the slow diffusion rate of Hf in certain minerals (e.g., zircons) (Cherniak et al., 1997), Hf isotopes of melt would be highly sensitive to the dissolution rate of these minerals, and such disequilibrium behavior of Hf presents an important caveat in the application of Lu–Hf isotopic system (Tang et al., 2014). In particular, the effect of isotopic disequilibrium between the partial melt and its magma source may be significant for Hf isotopic compositions of high-viscosity intermediate-felsic magmas because some minerals can crystallize over a long period in the crystal mush and may record transient compositions of fractional melt over time rather than the magmatic body or its magma source. In recent decades, owing to the rapid development of laser ablation multi-collector inductively couple plasma mass spectrometer (LA-MC-ICP-MS) that enabled fast and accurate Hf isotope analyses on small-sized samples, a large number of Hf isotopic studies were carried out on Hf-enriched minerals, such as zircon, baddeleyite, eudialyte, zirconolite and calzirtite (e.g., Wu et al., 2006, 2010; Bauer et al., 2017). Zircon is one of the most widely used minerals to infer primary $^{176}Hf/^{177}Hf$ compositions of magmas, owing to its high Hf concentration (commonly 0.5–2.0 wt%; Wu et al., 2006) and extremely low Lu/Hf ratio (typically ~0.002; Kinny and Maas, 2003). However, systematic studies are needed to examine the differences in Hf isotopes between zircons and their primary magma in order to correctly interpret the fast growing dataset of zircon Hf isotopes. Analyzing whole-rock samples is also suitable to acquire Hf isotopes. However, besides the difficulty in achieving complete decomposition of zircon-bearing rocks, a few other caveats need to be considered when using zircon or whole-rock Hf isotopic compositions to infer those of the magma or the source.

It has been noted that Hf isotopic compositions in zircons from many magmatic bodies (in particular intermediate-felsic intrusions) show larger ranges of variations than analytical uncertainties, even

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within individual hand specimens (e.g., Tang et al., 2014). These variations have been attributed to four potential reasons: (1) different zircons may have crystallized from different batches of melts with different Hf isotopic compositions during the melt accumulation process of intermediate–felsic magmas (e.g., Kemp et al., 2007; Shaw and Flood, 2009); (2) when partial melting happens at a low temperature and/or over a short time period, zircons could be inherited from the source (of the protolith) and they may not be fully dissolved so that the acquired whole-rock Hf isotopes would be biased to infer Hf isotopic compositions of primary melt (e.g., Mahar et al., 2016); (3) under high-grade metamorphism, transient metamorphic fluids could impart their Hf isotope compositions on all or part of zircons during zircon growth or overgrowth (e.g., Zheng et al., 2005); and (4) during magma mixing or crustal assimilation, zircons may record Hf isotopic compositions of the evolving melt while solidified magmas represent a final integrated composition (e.g., Boss, 2008; Yang et al., 2015; Couzinié et al., 2016). As Hf isotopic compositions in zircon could be affected by these magmatic processes, they may not simply be coupled with those of the whole-rock. Results from Ti-in-zircon thermometer indicate that magmatic zircons could crystallize over a long period during magmatic evolution (e.g., Harrison et al., 2007). More importantly, high precision single crystal CA-ID-TIMS ages demonstrate very convincingly the crystallization of magmatic zircon over a protracted time period in single magmas (e.g., Glazner et al., 2004; Schoene et al., 2012; Barboni et al., 2015; Szymanowski et al., 2017). Even in high-temperature low-viscosity ultramafic-mafic magmas, magmatic zircons may not record Hf isotopic compositions of the primary melt, because they tend to crystallize later during magma evolution and record progressive contamination (Wang et al., 2016).

To accurately interpret zircon Hf isotopic data, it is necessary to evaluate the effects of these processes on the coupling and decoupling of Hf isotopic compositions between zircons and their host rocks. To this end, we carried out two studies: (1) dissolution experiments to ensure total dissolution of whole-rock samples and confirm the effect of disequilibrium melting on Hf isotopic compositions; and (2) a case study to compare zircon vs. whole-rock Hf isotopic analyses of the Neoproterozoic Jiuling batholith of southern China.

2. Geological background and sample descriptions

The Jiuling batholith is located in the eastern part of Jiangnan Orogen. It is the largest Neoproterozoic granitic intrusion in southern China (Fig. 1a), with an exposed area of more than 2500 km^2 (Wang et al., 2013a and references therein) and zircon U–Pb ages of 835–810 Ma (e.g., Li et al., 2003; Wang et al., 2013a; Zhao et al., 2013). The Jiuling batholith could be divided into three units based on lithology and mineral size: Jiuxiantang (JXT), Shihuajian (SHJ) and Jiuling (JL) units (Fig. 1b). The JL unit is composed of medium- and coarse-grained granodiorites (35–55% plagioclase, 25–35% quartz, 3–15% K-feldspar, 5–15% biotite, 0–5% cordierite and 0–5% garnet). The SHJ unit is also composed of granodiorites, but, with fine grains. The SHJ granitoids show mineral assemblages of 40–55% plagioclase, 25–35% quartz, 5–40% K-feldspar, 5–10% biotite and 0–5% cordierite. In comparison, the JXT unit is composed of tonalites, with mineral assemblages of 40–55% plagioclase, 25–35% quartz, 2–7% K-feldspar and 10–15% biotite. Biotite is the dominant mafic minerals for the rocks and no hornblende has been observed in the batholith. Twenty-three granitoids samples were collected from the Jiuling batholith. The granitic rocks of the Jiuling batholith are overall homogeneous with SiO_2 contents of 65.2–71.2 wt% (Li et al., 2003). Locally we can see some microgranular enclaves, and they were suggested to represent mixing of supracrustal melts (i.e. partial melting of sedimentary rocks) (Zhao et al., 2013) or xenoliths of metasedimentary rocks (Xu et al., 1993). Only four granitic samples (09JL-06-1, 09JL-08-1, 09JL-14-2 and 07JL-06-2) were taken from the outcrops where some enclaves can be observed. Some garnets were observed in samples 11JL-04, 11JL-06-1, 11JL-16, 11JL-19 and 11JL-21, and some cordierites were observed in samples 09JL-08-1 and 07JL-06-2. The appearance of garnet and cordierite could also indicate the incorporation of supracrustal materials (e.g. sedimentary rocks) (Wang et al., 2013a).

To carry out the decomposition experiments, we selected five samples with mafic–felsic lithology based on preliminary data. One gabbroic sample (11ZJ-10-1) was collected from the Huangshan pluton in northwestern Zhejiang Province (ca. 820 Ma; Wang et al., 2012). One gabbroic sample (08XL-10-1) and one dioritic sample (08XL-06-4) were collected from the Xialan complex in northern Guangdong Province (ca. 195 Ma; Yu et al., 2009). One dioritic sample (11JH-01-1) was selected from the Miaohou complex in central Zhejiang Province (ca. 830 Ma; Xia et al., 2015). One granitic standard (GSR-1 from the Institute of Geophysical and Geochemical Exploration, China) was from the Qianlishan granitic pluton of southern Hunan Province (ca. 150 Ma; Li et al., 2004). These samples were selected and used in the decomposition experiments because the CL images and geochronological data have shown that they contain very rare old zircon xenocrysts or inherited zircons which make them suitable for the evaluation of the effect of disequilibrium partial melting processes. A summary of the ages, petrography and geochemistry for each of the representative samples are listed in Table 1.

3. Analytical methods

For zircon Hf isotope analysis, zircon grains were separated from crushed samples using conventional heavy liquid and magnetic techniques, mounted in epoxy resin and polished down to approximately half-section thickness to expose the grain centers. Isotopic and concentration analyses were carried out based on cathodoluminescence (CL) images as well as transmitted and reflected light micrographs. CL images were taken using a Mono CL3 + (Gatan, USA) attached to a scanning electron microscope (Quanta 400 FEG) at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an.

3.1. Zircon U–Th–Pb and trace element concentration

Zircon trace element concentrations and U–Th–Pb isotopic compositions were mostly analyzed using an Agilent 7500a ICP-MS attached to a New Wave 213 nm laser ablation system (later attached to a GeoLas Pro 193 nm laser ablation system) at the State Key Laboratory for Mineral Deposits Research, Nanjing University (MiDeR-NJU), following the procedures of Wang et al. (2007). Few LA-ICP-MS zircon U–Pb dating were also conducted at Shandong Bureau of China Metallurgical Geology Bureau. To correct U–Pb fractionation, zircon standard GEMOC GJ-1 ($^{207}Pb/^{206}Pb$ age of 608.5 ± 1.5 Ma; Jackson et al. 2004) was measured. NIST-612 glass was used for trace element concentration calculation with ^{29}Si as the internal standard. Zircon Mud Tank standard (732 ± 5 Ma; Black and Gulson, 1978) and basalt glass standard KL2G (Kilauea tholeiite; Jochum et al., 2000) were routinely analyzed to ensure age and trace element concentration accuracy, respectively. All analyses were carried out using a repetition rate of 5 Hz or 7 Hz. According to the size of zircon, the laser ablation beams were 25 μm or 35 μm in diameter. U–Pb ages were calculated using the on-line software package GLITTER (ver. 4.4) (Griffin et al., 2008; www.mq.edu.au/GEMOC). The common Pb correction was carried out through the Excel program of CompbCorr#3_15G (Andersen, 2002). U–Th–Pb age calculations and Concordia diagrams were generated using the ISOPLOT/Ex program (ver. 2.06) of Ludwig (1999).

3.2. Zircon Lu–Hf isotopes

After zircon U–Pb and trace element analyses, in situ zircon Lu–Hf isotopic analyses were obtained on the same spots or in the same domains as U–Pb analyses, using a New Wave ArF 193 nm laser ablation system attached to a Neptune plus multiple-collector inductively