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Research paper

A new approach for constraining the magnitude of initial disequilibrium in Quaternary zircons by coupled uranium and thorium decay series dating

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ABSTRACT

We have measured ^{238}U–^{206}Pb, ^{235}U–^{207}Pb, and ^{232}Th–^{208}Pb ages on Quaternary zircons by laser ablation, single-collector, magnetic sector inductively coupled plasma mass spectrometry (LA-ICP-MS). To obtain reliable ages for Quaternary zircons, corrections for initial disequilibrium associated with deficits and excesses of both ^{230}Th and ^{231}Pa relative to secular equilibrium resulting from differential partitioning during zircon crystallization or source melting must be made. In contrast, the ^{232}Th–^{208}Pb decay system is clearly advantageous for samples affected by disequilibrium because the ^{232}Th decay system lacks long-lived intermediate daughter isotopes. Conventionally, the initial disequilibrium for the ^{238}U and ^{235}U decay series has been determined by the distribution ratio between the melt and zircon (i.e., $f_{Th/U} = (Th/U)_{Zircon}/(Th/U)_{Melt}$ and $f_{Pa/U} = (Pa/U)_{Zircon}/(Pa/U)_{Melt}$). In our study, these correction factors were determined from comparison of the measured ^{238}U–^{206}Pb and ^{235}U–^{207}Pb ages with ^{232}Th–^{208}Pb ages obtained for three zircons of known eruption and, in some cases, zircon crystallization ages (Kirigamine Rhyolite, Bishop Tuff, and Toga Pumice). The resulting correction factors are $f_{Th/U} = 0.19 \pm 0.14$ and $f_{Pa/U} = 3.66 \pm 0.89$ (Kirigamine Rhyolite), $f_{Th/U} = 0.24 \pm 0.20$ and $f_{Pa/U} = 3.1 \pm 1.2$ (Bishop Tuff), and $f_{Th/U} = 0.28 \pm 0.17$ and $f_{Pa/U} = 3.04 \pm 0.99$ (Toga Pumice). Although the uncertainties of these f values are relatively large, our results support the adequacy of the conventional approach for correction of initial disequilibrium. A recent study published results that apparently show zircon crystallization ages are younger than the eruption age of Bishop Tuff. It seems to be difficult to eliminate these discrepancies, even if the Th/U partitioning and disequilibrium generated during partial melting are taken into account for recalculation of its zircon age. However, magma chamber process and history of Bishop Tuff are too complex to obtain accurate zircon ages by U–Pb method. To overcome this, therefore, the Th–Pb zircon dating method is a key technique for understanding complex, pre-eruptive magma processes, and further efforts to improve its precision and accuracy are desirable.

1. Introduction

Zircon U–series chronometry is a key method for understanding the high-temperature cooling history of magmas (Schmitt, 2011), because it has a relatively high closure temperature (900–1000 °C; Cherniak and Watson, 2001) compared with other chronometers such as $^{40}Ar/^{39}Ar$ sanidine dating (<400 °C; Baadsgaard et al., 1961). Hence, the precise determination of the crystallization age of Quaternary zircons using U–Th–Pb methods is a widely used method of studying magmatic systems (e.g., Bacon et al., 2000; Chamberlain et al., 2014; Oberli et al., 2004; Schmitt, 2011; Schmitt et al., 2003; Simon and Reid, 2005; Simon et al., 2008, 2014). However, when U–Pb dating is applied to young zircons, there has long been concern about the effect of initial disequilibria

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associated with intermediate nuclides in the ^{238}U or ^{235}U decay series (Ludwig, 1977; Mattinson, 1973; Schärer, 1984; Wendt and Carl, 1985). Without correction for the initial disequilibrium, the resulting ^{238}U–^{206}Pb and ^{235}U–^{207}Pb ages will deviate systematically from the true ages. For example, in the case of the ^{238}U decay series, the contribution of initial disequilibrium can be corrected if the Th/U fractionation between zircon and melt, defined by the Th/U abundance ratio between the zircon and melt (i.e., $(Th/U)_{Zircon}/(Th/U)_{Melt}$), is known (Schärer, 1984). The $(Th/U)_{Zircon}$ value can be directly measured in the zircon, whereas $(Th/U)_{Melt}$ is estimated from the Th/U ratio of the bulk rock (Guillong et al., 2014; Reid et al., 1997; Schmitt et al., 2003), melt inclusions in host rocks (Crowley et al., 2007; Schmitt et al., 2003), or glass in volcanic ash (Matthews et al., 2015). However, it is widely recognized that Th and U could have been heterogeneously distributed in the magma and, moreover, that $(Th/U)_{Melt}$ could change with time due to the crystallization of U–Th-bearing minerals within the melts (Amelin and Zaitsev, 2002). These factors make it difficult to estimate the $(Th/U)_{Melt}$ at the time and site of zircon crystallization.

The ^{238}U–^{230}Th method is also useful for the determination of crystallization ages of very young minerals (Fukuoka, 1974; Fukuoka and Kigoshi, 1974; Reid et al., 1997). Using this method, zircon ages can be determined by the isochron method through direct measurement of ^{230}Th. Several studies have successfully dated Quaternary zircons by this method using secondary ionization mass spectrometry (SIMS) or laser ablation, multiple-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) (e.g., Bacon and Lowenstern, 2005; Bernal et al., 2014; Reid et al., 1997). Despite the obvious advantages of the ^{238}U–^{230}Th method, data from multiple analyses are required to define the isochron, meaning that chronological information cannot be derived solely from a single analysis, unless two point model isochrones (e.g., for zircon–melt) can be constructed. This means that the resulting age represents averaged information from the analyzed crystal(s), and it is difficult to discern the potential multi-stage crystallization history of a single crystal if, for example, Th/U in the melt is variable (Boehnke et al., 2016). In addition, the use of ^{238}U–^{230}Th dating is limited to ages of <0.4–0.5 Ma, as beyond this the minerals reach secular equilibrium.

In contrast, the ^{232}Th–^{208}Pb dating method is a potential alternative to U–Pb dating as it does not require correction for the initial disequilibrium effect (Harrison et al., 1995; Oberli et al., 2004). This is because the half-lives of ^{232}Th decay series nuclides are significantly shorter than 10 a. The nuclide with the longest half-life is ^{228}Ra ($t_{1/2} = 5.75$ a; Mays et al., 1962), meaning that any state of initial disequilibrium is erased on a much shorter time scale than the expected precision of the measured ages. Furthermore, this dating method has a broader range of applications than ^{238}U–^{230}Th dating. In this study, we use the ^{232}Th–^{208}Pb method to date three zircon samples separated from Quaternary volcanic rocks and tephras, and we demonstrate the utility of this approach for Quaternary geochronology. We also present and discuss a new approach for constraining the effects of initial disequilibrium in the U decay series based on a comparison between U–Pb and Th–Pb ages.

2. Samples

In this study, three zircon samples from volcanic rocks or tephras with relatively high uranium and thorium concentrations were selected for analysis (Table 1), as follows.

(1) A rhyolite (obsidian) from the Wadatouge region in Kirigamine ("Kirigamine Rhyolite"), Nagano, Japan (Oikawa and Nishiki, 2005) contains zircon with high uranium concentrations (ca. 9000 ppm). This rhyolite is a well-known geochemical reference material distributed as JR-1 by the National Institute of Advanced Industrial Science and Technology (AIST), Japan (Imai et al., 1995). It is also used as a reference material for fission-track dating of glass (JAS-G1; Balestrieri et al., 1998). An $^{40}Ar/^{39}Ar$ age of 0.945 ± 0.005 Ma for JAS-G1 glass and a zircon fission-track age of 0.94 ± 0.08 Ma have previously been reported for this rock (Kitada and Wadatsumi, 1995; Sugihara et al., 2009).

(2) Zircons with uranium concentrations of ca. 3000 ppm were separated from the Bishop Tuff, collected from the same outcrop as locality no. 1 (Inyo County, California, USA) described by Izett et al. (1970). Only pumice clasts from the lower part of an air-fall unit at the base of the Bishop Tuff were used, which corresponds to unit F1 described by Hildreth and Wilson (2007). A precisely determined ^{238}U–^{206}Pb age for Bishop Tuff zircons by Crowley et al. (2007) of 767 ± 1 ka is widely regarded as their crystallization age. However, the Bishop Tuff is a classic zoned deposit and, as such, it is important to relate the ages to the units the samples were collected from. Many studies have documented the heterogeneity of zircons in the Bishop Tuff (e.g., Chamberlain et al., 2014; Reid and Coath, 2000; Reid et al., 2011; Simon and Reid, 2005). Disequilibrium-corrected U–Pb ages for early erupted samples of the Bishop Tuff (766.6 ± 3.2 ka and 774 ± 10 ka for rims and cores of zircon, respectively; Chamberlain et al., 2014) are comparable with those reported by Crowley et al. (2007). In contrast, there are significant differences between published $^{40}Ar/^{39}Ar$ dates of the Bishop Tuff, with dates ranging from ca. 760 to 780 ka, as follows: 758.9 ± 3.6 ka (Sarna-Wojcicki et al., 2000), 767.4 ± 0.4 ka (Rivera et al., 2011), 778.0 ± 7.4 ka (Renne, 2013), and 780 ± 4 ka (Simon et al., 2014). The variability is due to differences in the calibration of the $^{40}Ar/^{39}Ar$ technique and the analytical protocols used in each study (Renne, 2013).

(3) The Toga Pumice is one of our in-house standards, for which both sanidine $^{40}Ar/^{39}Ar$ (0.42 ± 0.01 Ma: Uto et al., 2010) and zircon fission-track ages (0.42 ± 0.08 Ma; Kano et al., 2002) have been reported. The Toga Pumice zircon has an average uranium concentration of ca. 3000 ppm.

The nature of the analyzed samples, sampling localities, and previously reported radiometric ages are summarized in Table 1.

3. Analytical method

Zircons were separated from the volcanic rocks and tephras using standard mineral separation techniques. Most zircons from all the samples are euhedral and generally larger than 30 × 100 μm in size. All the zircon grains were mounted on a PFA sheet (0.25 mm thick). Prior to isotopic analysis, the surfaces of the zircon grains were carefully polished using diamond paste (3 and 1 μm). In–situ U–Th–Pb isotopic analyses were carried out using an ICP-MS (AttoM High Resolution-ICP-MS, Nu instruments, Wrexham, UK) coupled to an ArF Excimer laser ablation system (ESI NWR-193, Portland, USA). The laser was operated with a repetition rate of 8 Hz and a spot size of 25–35 μm. A two-volume cell (ESI, Portland, USA) was used throughout the measurements and ablation was carried out in a He atmosphere, utilizing a small volume cell (<1 cm^3) to reduce sample washout time. After the ablation cell, the He carrier gas was mixed with Ar gas, and the laser-disintegrated sample particles were delivered to the ICP ion source in a mix of He and Ar. In order to reduce elemental fractionation during