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LETTER

High-precision oxygen isotope analysis of picogram samples reveals 2 μm gradients and slow diffusion in zircon

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ABSTRACT

Ion microprobe analysis with a sub-micrometer diameter spot reveals a sharp, 2 μm gradient in oxygen isotope ratio proving that oxygen diffusion in zircon is slow even under prolonged high-grade metamorphism. The data are consistent with an oxygen diffusion coefficient of $10^{-23.5\pm1}$ cm^2/s. Furthermore, this gradient is found in a zircon that contains clear textural evidence of recrystallization in nearby regions. This finding shows that through careful textural and chemical analysis, primary information can be extracted from a zircon that has also undergone partial recrystallization. The oxygen isotope ratios found in zircon have been used to infer magmatic and pre-magmatic histories, including the presence of liquid water on the surface of earliest Earth. Recently, these interpretations have been questioned with the assertion that zircon may not retain its primary oxygen isotope signature through metamorphism. The slow diffusion confirmed by these results supports interpretations that assume preservation of magmatic compositions.

Keywords: Ion microprobe, SIMS, zircon, diffusion, oxygen isotopes, stable isotopes, granulites facies, migmatites

INTRODUCTION

Oxygen isotopic ratios are constant for primitive magmatic rocks from the Earth's mantle, but can be highly fractionated by low-temperature processes on its surface. Thus, δ^{18}O is a powerful tracer of recycled crust that has been buried and melted, especially if it interacted with liquid water at low temperatures before burial. The accessory mineral zircon found within these rocks can be dated using the U-Pb system and provides a temporal record of geochemical information (e.g., Hanchar and Hoskin 2003). Oxygen isotopes in zircon have been used to chronicle the maturation of Earth's crust throughout geologic time (Valley et al. 2005), elucidate the origins of granite (Kemp et al. 2007), monitor differentiation of lunar crust (Nemchin et al. 2006b), and demonstrate the presence of liquid water on the surface of Earth in the earliest Archean (Wilde et al. 2001; Mojzsis et al. 2001; Cavosie et al. 2005). Although the concordance of U-Pb geochronology provides robust tests to evaluate post crystallization alteration, the oxygen isotope system contains no such safeguards and its resistance to chemical and physical alteration must be evaluated by other means. In particular, the rate of oxygen exchange by diffusion in zircon during high-grade metamorphism remains uncertain, and the retention of primary δ^{18}O values is sometimes controversial.

Several studies have shown that zircons preserve primary magmatic values of δ^{18}O through episodes of metamorphism, magmatism, and hydrothermal alteration (Valley et al. 1994; Peck et al. 2003; Valley 2003). However, careful laboratory experiments to measure the rate of oxygen diffusion in zircon suggest that although zircon is extremely retentive of oxygen only in the absence of water; even a small amount of water greatly enhances the diffusion rate of oxygen (Watson and Cherniak 1997; Cherniak and Watson 2003). These experimental results have been broadly interpreted to suggest that igneous zircons that have undergone metamorphism do not retain any primary oxygen isotope information. In particular, the elevated δ^{18}O found in the Early Archean zircons from the Jack Hills, Western Australia has been described as the product of hydrothermal alteration or granulite metamorphism, and therefore not a primary magmatic feature (Whitehouse and Kamber 2002; Nelson 2004; Hoskin 2005; Nemchin et al. 2006a).

Analysis of U-Pb isotopes, trace elements, and δ^{18}O by ion microprobe (Secondary Ion Mass Spectrometer, SIMS) in 20–30 μm diameter domains of single zircons has recently become routine. At the 20 μm scale, multiple analyses of single zircon grains reveal heterogeneities in all geochemical systems of interest, often (but not always) correlated with growth zoning and recrystallization features visible in cathodoluminescence imaging (CL). For these reasons, Cavosie et al. (2006) correlated zoning to the location of analysis pits from different ion probe analyses of zircon, suggesting that even zircons with complicated histories of metamorphism and recrystallization may contain pristine domains that preserve primary compositions.

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ION MICROPROBE MEASUREMENT OF $\delta^{18}O$

The spot size used for oxygen isotope analysis by ion microprobe has decreased and analytical precision has improved in the last several years from ±1–2‰ (2 S.D.) on 30 μm diameter pits (e.g., Peck et al. 2003) to ±0.6‰ (2 S.D.) on 15 μm diameter pits (e.g., Cavosie et al. 2005). The development of the most recent generation of large radius, multicollector ion microprobes and refinement of procedures is allowing further improvement of precision and sample size. In this study we report analyses of $\delta^{18}O$ in zircon with 10, 7 μm, and sub-1μm spot size with spot-to-spot precisions of 0.3, 0.7, and 2‰, respectively (2 S.D.). The precisions reported here scale inversely with sample size, 300, 200, and 1–2 picograms (pg), respectively, and are largely controlled by the detection system: peak/background ratio for Faraday cups and the statistics of Poisson distribution of the number of atoms analyzed. These sample sizes are 10^6 to 10^9 smaller than those analyzed by conventional fluorination and mass-spectrometry techniques (pg vs. mg) for which precision of 0.1‰ is obtained (Valley et al. 1995). This method has yielded spot-to-spot precision as good as ±1.4‰ (2 S.D.), which approaches the physical limits of stable isotope analysis. These small spot sizes have allowed us to measure an oxygen diffusion profile in zircon, and to confirm that zircons with complicated magmatic and metamorphic histories can retain relatively pristine domains, unaltered by diffusion.

SAMPLE

The zircon that is the target of this study was separated from a metasediment (Sample BMH-04-01a, zircon 35) at the Daniel's Road locality near Saratoga Springs, New York (UTM 18T 0599340 4773619, WGS84, Bickford et al. in review), in the southeastern part of the granulite-facies Adirondack Highlands (Valley et al. 1990). It was chosen based on geochemical, petrologic, and textural criteria that suggested a low $\delta^{18}O$ core and high $\delta^{18}O$ rim. In addition, this zircon contains textural evidence of a zone of recrystallization along a healed fracture (Fig. 1) clearly indicating that portions of the core region of this zircon have been modified.

To maximize any diffusion profile, a large gradient in $\delta^{18}O$ is desirable. Zircons from primitive magmas are likely to have $\delta^{18}O$ close to the mantle range: 4.7 to 5.9‰ (Valley 2003). Clastic sediments typically have elevated whole rock $\delta^{18}O$ values (~10–20‰) as a result of chemical weathering. The zircon in this study is composed of a detrital igneous core, recognizable by fine-scale oscillatory zoning in CL (Fig. 1) and by its U-Pb ages (1353 Ma—core, 1019 Ma—rim, Bickford et al. in review). Oxygen isotope analysis by ion microprobe of neoformed zircon overgrowths (e.g., Fig. 1, dark CL) in migmatitic rocks throughout the Adirondacks reveals elevated $\delta^{18}O$ (8–10‰) consistent with in situ melting of the host metapelite during granulite facies metamorphism (Lancaster et al. 2006). Migmatites are found throughout the Adirondacks and preserve a record of the prolonged magmatic and metamorphic history (ca. 1350–1000 Ma, McLelland et al. 2004; Heumann et al. 2006; Bickford et al. in review) with peak metamorphic temperatures of 700–800 °C (Bohlen et al. 1985; Kitchen and Valley 1995; Spear and Markussen 1997; Peck and Valley 2004; Storm and Spear 2005).

ANALYTICAL METHODS

Initial $\delta^{18}O$ analyses were made with a CAMECA ims-1280 ion microprobe at the University of Wisconsin—Madison (WiscSIMS) using a 10 μm diameter analysis spot. Later analyses were made with a reduced beam size of 7 μm (Fig. 1b) following a method described by Kita et al. (2007b). Analyses were made in multicollection mode using dual Faraday cup detectors and a focused Cs^+ primary beam. The reproducibility of analyses (2 S.D.) on a homogeneous zircon standard (KIM-5) varied from 0.3 to 0.4‰ (10 μm spot) to 0.7‰ (7 μm spot). Sample analyses were bracketed by analyses of KIM-5 mounted <5 mm from the sample. Values of $\delta^{18}O$ are standardized to VSMOW and reported in standard per mil notation. Additional detail is provided in the Online Deposit. After each analysis session, the zircons and all analysis pits were imaged in CL and secondary electrons (SE) using a scanning electron microscope. Spot location was determined by SE and superimposed on the CL image (Fig. D1[1]). The shortest distance from the center point of each analysis pit to the CL boundary between core and rim was then measured.

Recent refinements of technique with the CAMECA ims-1280 instrument have led to improved precision and accuracy of oxygen isotope analysis in many applications (Kita et al. 2007a), including use of an analytical spot size that measures less than 1 μm^2. The instrument configuration[1] for sub-1μm analyses is similar to that detailed above but with a ca. 1 pA Cs^+ primary beam focused to less than 1 μm on a calibrated Si target and ^{18}O measured by an electron multiplier in the multicollection system rather than a Faraday cup. Analyses were standardized to the homogeneous

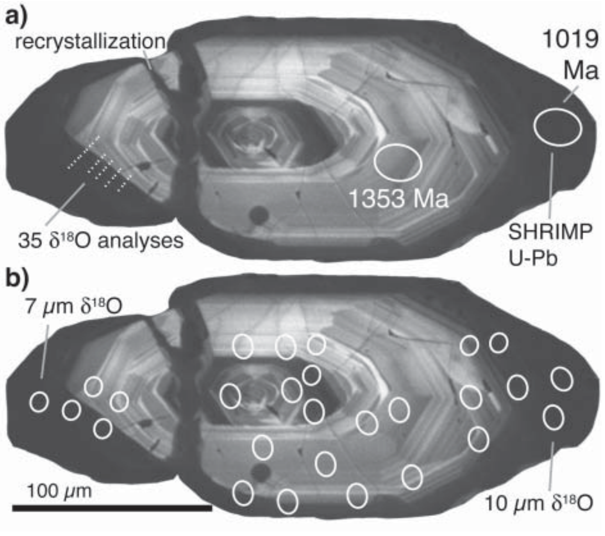

FIGURE 1. Cathodoluminescence (CL) image (surface 3) of the Adirondack zircon from this study showing bright oscillatory zoning in the igneous core region and darker zoning in the anatectic rim. A dark forked band cuts across the zircon marking a recrystallized fracture. (**a**) Location and size of 30 μm U-Pb analyses by Sensitive High-Resolution Ion Microprobe made on surface 1 (Bickford et al. in review) and sub-1μm $\delta^{18}O$ analyses made on surface 3. (**b**) Location and size of 10 and 7 μm oxygen isotope analyses made on surface 2. CL images of each surface analyzed show little change with polishing (Fig. D1, Online Deposit).

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[1] Deposit item AM-07-031, Online Deposit (High-precision oxygen isotope analysis of picogram samples reveals 2 μm gradients and slow diffusion in zircon, including Figs. D1–D3 and Table D1). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of the recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

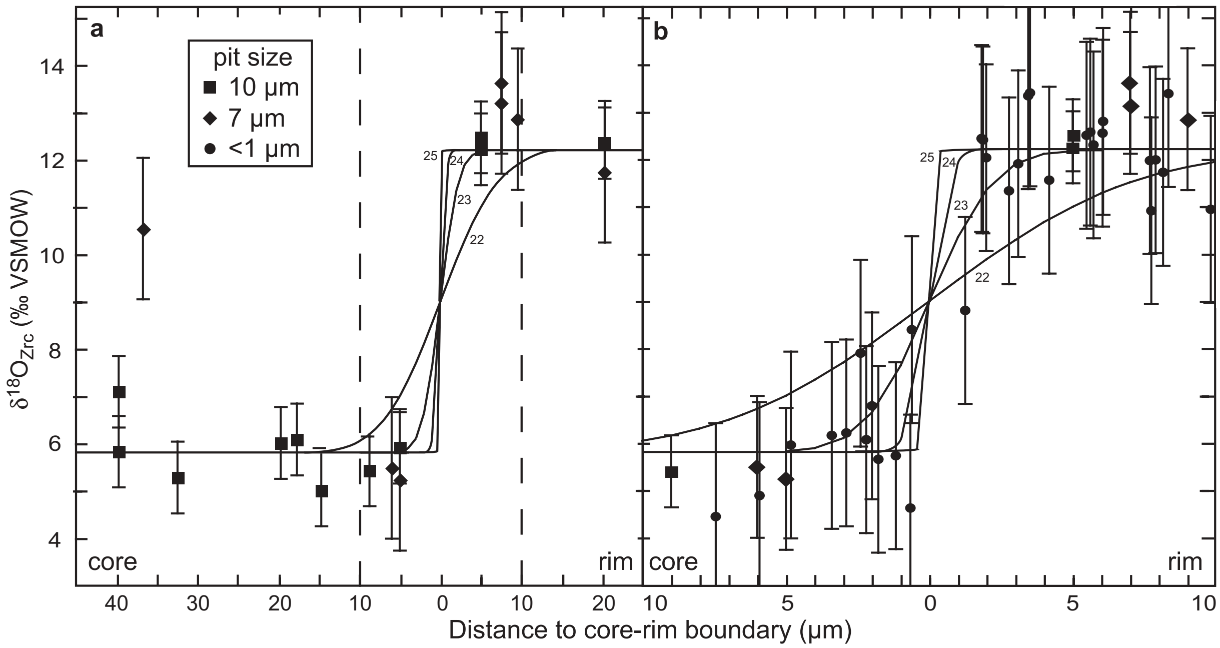

FIGURE 2. Oxygen isotope diffusion profiles measured in the zircon shown in Figure 1. Only those analyses that do not represent mixtures of core and rim material are shown (i.e., >1 beam radius from interface). Error bars are shown at the 95% confidence interval and represent the reproducibility of the KIM-5 zircon standard before and after each analysis session. Uncertainty in the position of the points is estimated at ~200 nm within 10 μm of the interface and may be as large as 3 μm far from the interface. (**a**) 10 and 7 μm spots for the full zircon showing a sharp increase in δ^{18}O from the core to the rim. Two spots with elevated δ^{18}O from the innermost core may represent an earlier generation of zircon, or a zone of late recrystallization, and are not included in the core average. Dashed lines indicate the region shown in **b**. (**b**) Data from within 10 μm of the core-rim interface including the sub-1μm spots. Calculated diffusion profiles for an isothermal period of 50 Myr labeled in –log D (cm^2/s). The data are consistent with a diffusion coefficient of $10^{-23.5\pm1}$ cm^2/s.

rim composition of the zircon defined by the 7 and 10 μm analyses. Additional details are available in the Online Deposit[1]. We have employed a spot measuring ca. 0.6 × 0.9 μm to make 35 analyses, ~2 μm apart, within 10 μm of the core-rim interface. The depth of these spots is constrained to 0.6 to 1.1 μm (depending on primary bean intensity) by estimates of sputter rate and by direct measurements on pits cut in cross-section by a focused ion beam/scanning electron microscope (Online Deposit[1]). Each analysis consumes ca. 1 to 2 pg of zircon.

RESULTS AND DISCUSSION

Twenty-seven analyses (both 10 and 7 μm pits) were made throughout the core and rim regions of the Daniel's Road Adirondack zircon (Fig. 1b, Table D1). Seven analysis pits that were found in a post analysis examination by scanning electron microscope to lie on cracks in the zircon were excluded. The average core composition (analyses ≥ 1 pit radius from the CL boundary) is δ^{18}O = 5.5‰, the rim is 12.6‰. It is readily apparent that the oxygen isotope gradient between core and rim is quite sharp and cannot not be resolved even with the smaller 7 μm spot (Table D1, Fig. 2a). Two analyses (not on cracks) that overlap the core-rim CL boundary represent mixtures between the two compositions and are not plotted in Figure 2 for clarity. The sample was then polished to remove the existing ~1 μm deep analysis pits, and an additional 35 sub-1μm diameter analyses were made across the core-rim interface where the oxygen isotope gradient is steep, but diffusive exchange was not previously resolved due to larger analysis spots (Fig. 1b). In spite of the somewhat larger uncertainty of these new data (±2.0‰, 2 S.D.) the small spot size reveals that over 50% of the oxygen isotope exchange is restricted to within ~2 μm of the contact that is imaged in CL (Table D1, Fig. 2b). The average core composition based on 10, 7, and sub-1 μm analyses is 5.8‰ and the rim composition is 12.2‰.

Hypothetical diffusion profiles for δ^{18}O in the immediate region of the core/rim interface of the zircon were calculated using the non-steady-state solution for diffusion in an infinite composite medium (Equations 3.45 and 3.46 of Crank 1975), and assuming a 50 Myr isothermal period (e.g., Mezger et al. 1991; Peck et al. 2003). Because diffusion is modeled close to the interface relative to the size of the zircon, the isothermal and one-dimensional models are good approximations. The data are consistent with an oxygen diffusion coefficient of $10^{-23.5\pm1}$ cm^2/s (Fig. 2b) for the 50 Myr duration of granulite facies metamorphism estimated from zircon geochronology. Even if the zircon remained at peak temperature for only 5 Myr and had not cooled slowly, D is still constrained to less than 10^{-21} cm^2/s. These results are consistent with the water-absent experiments of Watson and Cherniak for temperatures of 700–750 °C, but diffusion is much slower than observed in the water-present experiments at the same temperatures (Watson and Cherniak 1997). The preservation of such a sharp profile in a metamorphosed zircon and the low value of the diffusion coefficient that is inferred indicate that domains with pristine oxygen isotope ratio should commonly be preserved and that high-grade metamorphism should not be assumed to reset δ^{18}O. Furthermore, our preliminary studies of zircons from other high-grade terranes including upper amphibolite facies (Lancaster et al. 2006) and high-temperature (700–800 °C) eclogites (Fu et al. 2006) show similar steep gradients within single zircons at the sub-10μm scale, suggesting that if zircons are carefully studied with correlated imaging and spot analysis, then the preservation of this important geochemical information can be interpreted with confidence.

This finding is particularly important for the interpretation of the Early Archean (>4 Ga) zircons that represent the oldest terrestrial material available for study. Although no evidence of rapid oxygen diffusion in Early Archean zircons has yet been presented, these zircons do not have the extreme range in δ^{18}O required to test this possibility using the method presented in this study. It has been suggested that evidence of recrystallization in one portion of a zircon due to metamorphism makes all data obtained from that zircon unreliable (Nemchin et al. 2006a). The presence of a resolvable oxygen diffusion profile consistent with extremely slow diffusion less than 20 μm away from a zone of recrystallization (Fig. 1b) in the Daniel's Road zircon makes this assertion highly questionable.

We also note that the ability to analyze oxygen isotope ratios from 1 μm spots with per mil precision opens new and exciting opportunities to investigate stable isotope chemistry in materials that are small, precious, or zoned, including many of biological origin.

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