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Primitive oxygen-isotope ratio recorded in magmatic zircon from the Mid-Atlantic Ridge

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Abstract

The oxygen-isotope composition of the Earth's upper mantle is an important reference for understanding mantle and crust geochemical cycles. Olivine is the most commonly used mineral for determining the influence of crustal processes on the oxygen-isotope ratio ($\delta^{18}O$) of primitive rocks, however it is an uncommon mineral in continental crust and readily alters at or near Earth's surface. Here we report the first measurements of oxygen-isotope ratios in zircon from oceanic crust exposed at a mid-ocean ridge. Measurements of $\delta^{18}O$ and trace elements were made by ion microprobe on zircon in polished rock chips of gabbro and veins in serpentinized peridotite drilled from the Mid-Atlantic Ridge. The zircon grains contain both oscillatory and sector growth zoning, features characteristic of magmatic zircon. Values of $\delta^{18}O$ (zircon) = 5.3 ± 0.8‰ (2 st. dev., n = 68) for the population are consistent with the interpretation that these grains are igneous in origin and formed in high-temperature isotopic equilibrium with mantle oxygen. The $\delta^{18}O$ values demonstrate that zircon in oceanic crust preserves primitive $\delta^{18}O$ in spite of sub-solidus alteration of the whole rock. The fact that the primitive $\delta^{18}O$ (zircon) values fall in a narrow range (5.3 ± 0.8‰) strengthens the use of oxygen isotopes in zircon as a tracer to identify processes of exchange in a wide range of modern and ancient crustal environments, including subducted oceanic crust (eclogite), and also in the oldest known pieces of Earth, >3900 million-year-old detrital zircon grains from Western Australia.

Keywords: Zircon, ODP, MARK, oxygen isotope, oceanic crust, ion microprobe

Introduction

Geochemical interactions between the crust and mantle at mid-ocean ridges and subduction zones influence global chemical cycling. New, predominantly mafic crust is intermittently generated at ocean spreading centers from sub-axial intrusions of basaltic magma beneath ridges. In this environment, both low- and high-temperature fluids commonly alter the primary oxygen-isotope ratio ($\delta^{18}O$) of newly formed rocks, a process that imparts "crustal" (i.e., non-mantle) $\delta^{18}O$ values to newly formed oceanic crust, and buffers the $\delta^{18}O$ of seawater in the process (Muehlenbachs and Clayton 1976; Gregory and Taylor 1981; Muehlenbachs 1986; Jean-Baptiste et al. 1997). Given the susceptibility to alteration, the study of magmatic oxygen-isotope ratio in oceanic crust thus requires the existence of a mineral that will reliably preserve magmatic compositions. Whereas olivine is typically the mineral of choice for detecting contributions of crust-derived oxygen in primitive low-SiO_2 rocks (Mattey et al. 1994; Eiler et al. 1996; Eiler 2001), the use of olivine as an oxygen-isotope monitor is somewhat limited, as it is uncommon in evolved rocks and readily alters at or near the Earth's surface. In contrast, zircon is a common mineral in felsic rocks and is increasingly being recognized in mafic rocks. In addition, it is highly resistant to erosion and can provide a reliable record of the primary $\delta^{18}O$ composition of melts with complicated histories (Valley et al. 2005). Furthermore, zircon grains carry a range of other geochemical information that can be combined with $\delta^{18}O$ to determine the genesis of parent rocks (Hoskin and Schaltegger 2003; Valley 2003).

The use of $\delta^{18}O$ (zircon) to detect the effects of crustal processes affecting magma compositions requires knowledge of the $\delta^{18}O$ value of zircon in equilibrium with mantle oxygen. The mantle-equilibrated value for $\delta^{18}O$ (zircon) of 5.3 ± 0.6‰ (2 standard deviations, st. dev.) is thus far only known from measurements of xenocrystic zircon entrained in kimberlite (Valley et al. 1998; Page et al. 2007). Here, we report oxygen-isotope measurements by ion microprobe of zircon in igneous rocks from modern oceanic crust.

Mid-Atlantic Ridge geology

The Mid-Atlantic Ridge is a slow spreading center, with a full spreading rate of ~25 mm/year (Shipboard Scientific Party 1995a). The structure of oceanic crust along the Mid-Atlantic Ridge is highly variable, and shows significant differences in both thickness and composition compared to the classic view of layered oceanic crust, which features horizontal contacts between the overlying sediments, extrusive basalts, sheeted dikes, layered and isotropic gabbros, and underlying ultramafic rocks (Snow 1995; Karson 1998). The presence of serpentinized ultramafic rocks in early dredge hauls was one of the first indications that anomalous crustal sections that expose underlying upper mantle rocks occur along the Mid-Atlantic Ridge (e.g., Prinz et al.

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1976). So-called "anomalous" crustal structures have now been documented in many locations along the global mid-ocean ridge system (Karson 1998).

Ocean-floor drilling during Leg 153 of the Ocean Drilling Program (ODP) recovered gabbros and serpentinized ultramafic rocks from five sites south of the Kane Transform on the west flank of the Mid-Atlantic Ridge (MARK area), between 23°15′N and 23°35′N (Shipboard Scientific Party 1995a). Drilling at sites 921–924 (~5 km south of the Kane Transform) primarily recovered gabbroic samples, whereas at site 920, (~18 km further south) serpentinized peridotites with minor gabbro were recovered (Fig. 1). Zircon grains have been found in samples from each site drilled during Leg 153 (Cannat et al. 1997; Dilek et al. 1997; Pilot et al. 1998; Shipboard Scientific Party 1995b), as well as in other samples along the Mid-Atlantic Ridge, e.g., 15°37′N, (Cannat et al. 1992). If the occurrence of zircon described thus far from fast- and slow-spreading environments is representative of mid-ocean ridges, zircon appears to be a ubiquitous trace phase in oceanic crust. In addition to the Mid-Atlantic Ridge, zircon has been reported as an accessory mineral in oceanic crust from other areas, including the Southwest Indian Ridge (Dick et al. 1991; Stakes et al. 1991; Vanko et al. 1991; John et al. 2004; Schwartz et al. 2005), the East Pacific Rise (Shipboard Scientific Party 1993; Kelley and Malpas 1996), and the Iberian Peninsula (Beard et al. 2002; Gardien and Paquette 2004).

Samples and methods

Twenty-four zircon samples from Leg 153, including one gabbro (sample 153-922B-2R-2, 20–23 cm) and two serpentinite samples (samples 153-920B-2R-1, 44–50 cm and 153-920B-5R-1W, 59–64 cm) were analyzed for $\delta^{18}O$ in-situ in polished rock chips using a CAMECA IMS-1280 ion microprobe at the Wisc-SIMS Laboratory at the University of Wisconsin-Madison (see methods, Appendix 1[1]). Four Leg 153 serpentinite whole rocks (samples from holes 920B and 920D) were analyzed for $\delta^{18}O$ by laser fluorination gas-source mass spectrometry at the University of Wisconsin-Madison (see methods, Appendix 1[1]). Analyses of zircon trace elements, including Ti, Y, Hf, and rare-earth elements were also made with the Wisc-SIMS IMS-1280 on seven grains (see methods, Appendix 1[1]). The zircon grains in these samples are generally large (>100 μm), polished to a smooth, low-relief surface (few cavities or fluid inclusions), and most preserve sector or oscillatory zoning in cathodoluminescence (Fig. 2). Mineral inclusions of plagioclase, apatite, and both Fe and Fe-Ti oxide were identified in several grains (Valley and Cavosie 2006). Zircon in gabbroic samples occurs along grain boundaries and as inclusions, contains both oscillatory and sector igneous growth zoning (Fig. 2), and thus appears texturally to be a magmatic phase. Interpreting the textural occurrence of zircon in the serpentinite samples is complicated by the extensive hydrothermal alteration of the host peridotite. Most zircon grains are found in millimeter- to centimeter-scale altered dikes within the serpentinites that were introduced after magmatic intrusion of the peridotite and prior to serpentinization. In serpentinite sample 153-920B-2R-1 (interval 44–50 cm), zircon is found in a centimeter-scale dike that is now altered; zircon and apatite are the only preserved magmatic phases, and are surrounded by secondary actinolite ± carbonate. Zircon in this sample appears to have formed during intrusion of the serpentinite by a felsic melt, and is not an equilibrium matrix phase. In the other serpentinite sample investigated (153-920B-5R-1W, interval 59–64 cm), zircon occurs in millimeter-scale secondary veins and dikes.

[1] Deposit item AM-09-033, Appendix 1. 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 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.

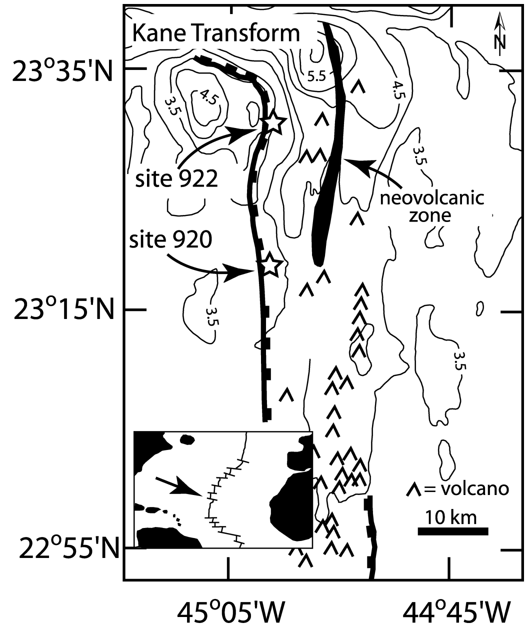


Figure 1. Map of MARK area (Mid-Atlantic Ridge, Kane Transform), after Shipboard Scientific Party (1995). Bathymetry contours listed in kilometers below sea level. The Leg 153 sites (920–924) are located between 23°15′N and 23°35′N.

Results

Sixty-eight analyses of $\delta^{18}O$ (zircon) were made on the three Mid-Atlantic Ridge samples (Fig. 2; Table 1). Most grains are relatively homogeneous and show small intra-grain variations, with standard deviations similar to analyses of standard KIM-5 on the same mount (Table 1). Only two zircon samples, one from each serpentinite sample, showed intra-grain variability that exceeded that found for standard KIM-5 (Fig. 2). No consistent zonation in $\delta^{18}O$ was detected for core-rim relations, or in sector zoned grains; some grains yield slightly higher $\delta^{18}O$ in dark CL sectors, whereas other grains yield slightly lower $\delta^{18}O$ in dark CL sectors. Gabbro sample 153-922B-2R-2 (interval 20–23 cm) yielded an average $\delta^{18}O$ (zircon) = 5.3 ± 0.4‰ (n = 32 analyses on 14 grains). Serpentinite sample 153-920B-2R-1 (interval 44–50 cm) yielded an average $\delta^{18}O$ (zircon) = 5.0 ± 0.8‰ (n = 20 analyses on 7 grains). Serpentinite 153-920B-5R-1W (interval 59–64 cm) yielded an average $\delta^{18}O$ (zircon) = 5.5 ± 0.7‰ (n = 16 analyses on 3 grains). The average of the 68 analyses is 5.3 ± 0.8‰ (VSMOW, 2 st. dev.) (Fig. 3a; Table 1). This value is indistinguishable from the value of $\delta^{18}O$ = 5.3 ± 0.6‰ (2 st. dev.) for zircon in high-temperature equilibrium with mantle melts determined by analysis of much larger samples of kimberlite zircon (Valley et al. 1998; Valley 2003; Page et al. 2007) and also olivine in ocean floor basalt (Mattey et al. 1994; Eiler et al. 1996) using accurate and precise laser fluorination techniques. A Student's t-test to compare the population of $\delta^{18}O$ values from each of the three samples with mantle-equilibrated zircon ($\delta^{18}O$ = 5.3 ± 0.6‰) shows that the sample means are indistinguishable from mantle zircon at a significance level of 0.01 (gabbro: p = 0.95; serpentinites: p = 0.03 to 0.24).

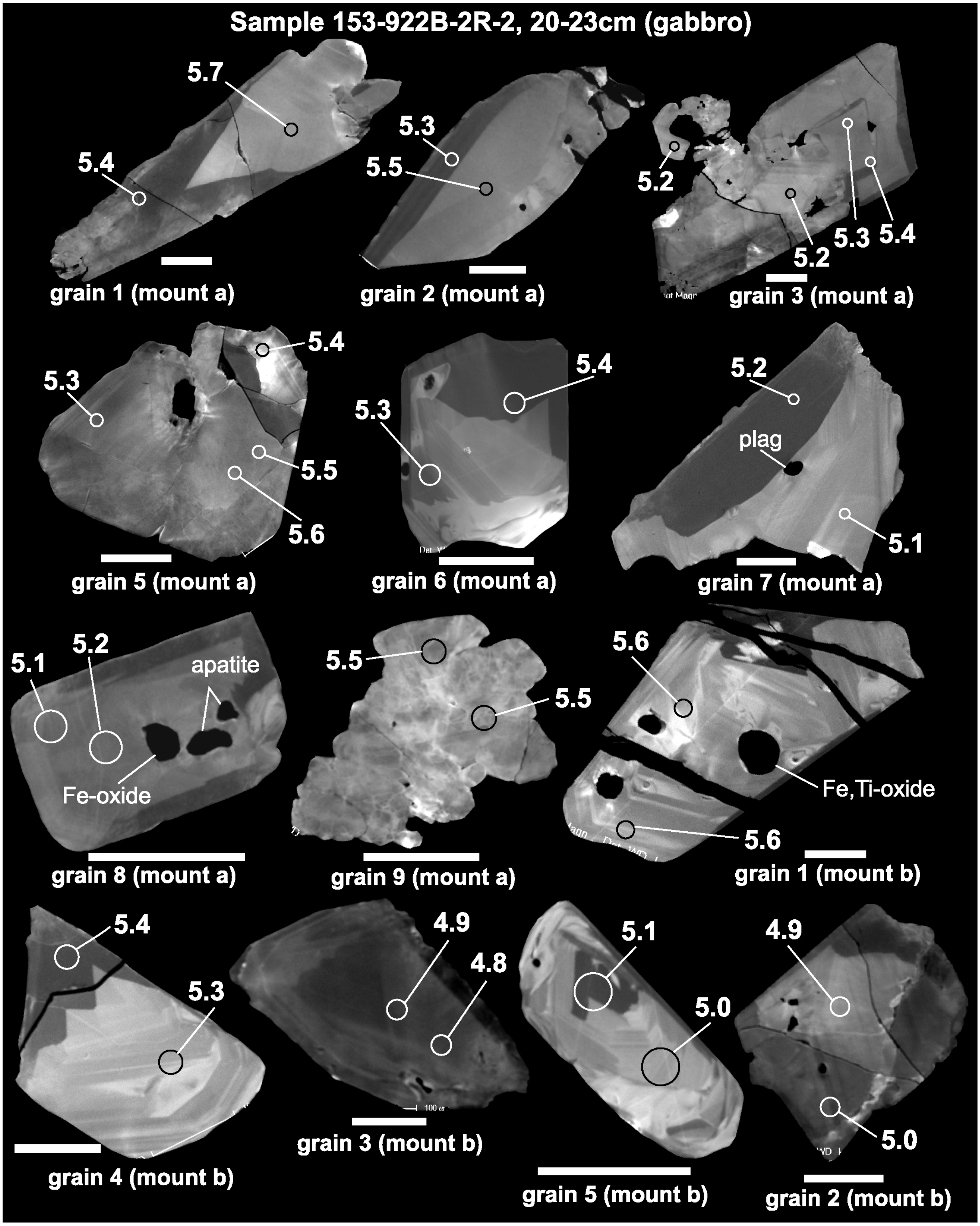


FIGURE 2. Cathodoluminescence images of representative Leg 153 zircon grains analyzed in this study. Oxygen-isotope analysis locations and values (VSMOW) are indicated. Scale bars are 50 µm. *Continued on next page.*

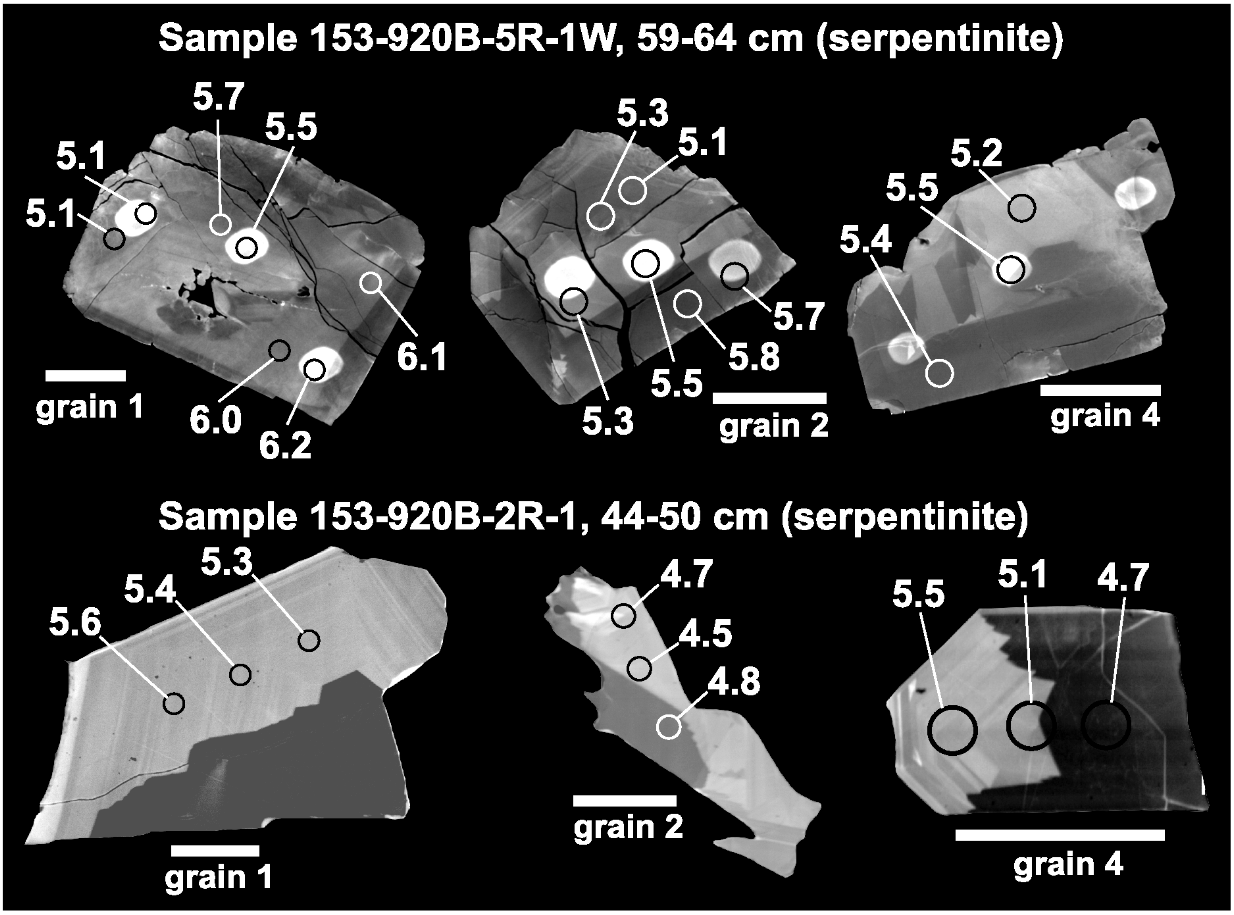
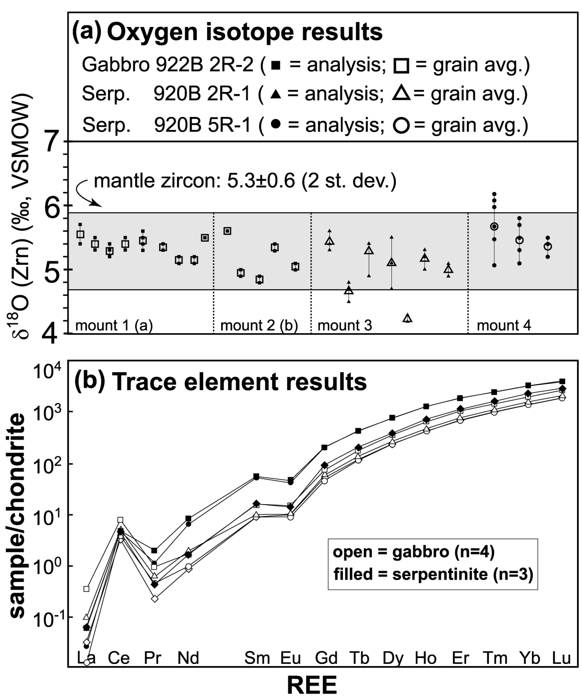


FIGURE 2. *Continued.*



Normalized rare-earth element (REE) abundances from 6 zircon grains in Leg 153 gabbro and serpentinite (Fig. 3b; Table 2) show typical characteristics for crustal zircon, including a positive Ce and negative Eu anomalies, and an overall enrichment in HREE over LREE. In addition, the MARK zircon grains overlap zircon found in a wide compositional range of crustal igneous rocks (Hoskin and Ireland 2000), as well as oceanic crust (Grimes et al. 2007). Titanium abundances (18.1 to 36.9 ppm) measured in the same grains suggest apparent (uncorrected) crystallization temperatures from 796 to 870 °C based on Ti-saturation thermometry (Watson and Harrison 2005; Table 2). Whole-rock $\delta^{18}O$ values for four Leg 153 serpentinites range from 2.88 to 3.56‰ (Table 3).

◀**FIGURE 3.** Ion microprobe data for Leg 153 zircon samples. (**a**) Oxygen-isotope ratios ($\delta^{18}O$) for zircon grains from gabbro and dikes in serpentinite. Each vertical array (connected by a tie-line) consists of analyses from a single grain. The small symbols are individual analyses; the larger symbol is the grain average. The shaded area with value of 5.3 ± 0.6‰ (2 st. dev.) indicates the range for zircon in high-temperature equilibrium with primitive mantle $\delta^{18}O$ (Valley 2003). Analytical uncertainty ranges from ±0.1 to ±0.5‰ (2 st. dev.) for the four mounts (Table 1). (**b**) Chondrite-normalized rare earth element (REE) data for zircon grains from gabbro and serpentinite.

Table 1. Oxygen-isotope analyses of zircon from ocean crust by CAMECA IMS 1280 ion microprobe

Gabbro: 153-922B-2R-2, 20–23 cm (mount "a")

Analysis*	$^{18}O/^{16}O_{(meas)}$	$\delta^{18}O$ (VSMOW)
KIM-5	2.0183E-03	–
KIM-5	2.0186E-03	–
KIM-5	2.0182E-03	–
KIM-5	2.0183E-03	–
KIM-5	2.0183E-03	–
KIM-5	2.0177E-03	–
KIM-5	2.0181E-03	–
KIM-5	2.0180E-03	–
KIM-5	2.0181E-03	–
KIM-5	2.0183E-03	–
Zircon 5, spot 1	2.0186E-03	5.5
Zircon 5, spot 2	2.0189E-03	5.6
Zircon 5, spot 3	2.0185E-03	5.4
Zircon 5, spot 4	2.0182E-03	5.3
Zircon 6, spot 1	2.0185E-03	5.4
Zircon 6, spot 2	2.0182E-03	5.3
Zircon 7, spot 1	2.0179E-03	5.1
Zircon 7, spot 2	2.0181E-03	5.2
KIM-5	2.0175E-03	–
KIM-5	2.0176E-03	–
KIM-5	2.0175E-03	–
Zircon 9, spot 1	2.0187E-03	5.5
Zircon 9, spot 2	2.0186E-03	5.5
Zircon 8, spot 1	2.0181E-03	5.2
Zircon 8, spot 2	2.0178E-03	5.1
Zircon 4, spot 1	2.0187E-03	5.5
Zircon 4, spot 2	2.0182E-03	5.3
KIM-5	2.0176E-03	–
KIM-5	2.0176E-03	–
Zircon 3, spot 2	2.0185E-03	5.4
Zircon 3, spot 3	2.0183E-03	5.3
Zircon 3, spot 4	2.0181E-03	5.2
Zircon 3, spot 5	2.0181E-03	5.2
Zircon 1, spot 1	2.0190E-03	5.7
Zircon 1, spot 2	2.0185E-03	5.4
Zircon 2, spot 1	2.0187E-03	5.5
Zircon 2, spot 2	2.0182E-03	5.3
KIM-5	2.0175E-03	–
KIM-5	2.0176E-03	–
KIM-5	2.0176E-03	–
KIM-5 avg	2.0179E-03	–
KIM-5 std dev (2σ)	3.61866E-07	0.4‰

Gabbro: 153-922B-2R-2, 20–23 cm (mount "b")

Analysis*	$^{18}O/^{16}O_{(meas)}$	$\delta^{18}O$ (VSMOW)
KIM-5	2.0186E-03	–
KIM-5	2.0184E-03	–
KIM-5	2.0185E-03	–
KIM-5	2.0183E-03	–
Zircon 5, spot 1	2.0184E-03	5.0
Zircon 5, spot 2	2.0185E-03	5.1
Zircon 4, spot 1	2.0190E-03	5.3
Zircon 4, spot 2	2.0192E-03	5.4
Zircon 3, spot 1	2.0181E-03	4.9
Zircon 3, spot 2	2.0179E-03	4.8
Zircon 2, spot 1	2.0181E-03	4.9
Zircon 2, spot 2	2.0183E-03	5.0
Zircon 1, spot 1	2.0195E-03	5.6
Zircon 1, spot 2	2.0195E-03	5.6
KIM-5	2.0187E-03	–
KIM-5	2.0185E-03	–
KIM-5	2.0188E-03	–
KIM-5	2.0186E-03	–
KIM-5 avg	2.0185E-03	–
KIM-5 std dev (2σ)	2.8756E-07	0.1‰

Notes: meas = measured; avg = average; std dev = standard deviation.
* Analyses listed in sequence made.

Table 1.—Continued

Serpentinite: 153-920B-2R-1, 44–50 cm

Analysis	$^{18}O/^{16}O_{(meas)}$	$\delta^{18}O$ (VSMOW)
KIM-5	2.0191E-03	–
KIM-5	2.0200E-03	–
KIM-5	2.0182E-03	–
KIM-5	2.0176E-03	–
KIM-5	2.0180E-03	–
KIM-5	2.0186E-03	–
KIM-5	2.0187E-03	–
KIM-5	2.0184E-03	–
KIM-5	2.0177E-03	–
KIM-5	2.0180E-03	–
KIM-5	2.0175E-03	–
KIM-5	2.0187E-03	–
KIM-5	2.0188E-03	–
KIM-5	2.0183E-03	–
KIM-5	2.0180E-03	–
KIM-5	2.0186E-03	–
Zircon 2, spot 1	2.0173E-03	4.5
Zircon 2, spot 2	2.0177E-03	4.7
Zircon 2, spot 3	2.0177E-03	4.8
Zircon 3, spot 1	2.0191E-03	5.4
Zircon 3, spot 2	2.0191E-03	5.4
Zircon 3, spot 3	2.0181E-03	4.9
Zircon 3, spot 4	2.0191E-03	5.4
Zircon 4, spot 1	2.0192E-03	5.5
Zircon 4, spot 2	2.0185E-03	5.1
Zircon 4, spot 3	2.0176E-03	4.7
KIM-5	2.0180E-03	–
KIM-5	2.0182E-03	–
KIM-5	2.0184E-03	–
KIM-5	2.0185E-03	–
KIM-5	2.0184E-03	–
KIM-5	2.0182E-03	–
Zircon 1, spot 1	2.0191E-03	5.4
Zircon 1, spot 2	2.0188E-03	5.3
Zircon 1, spot 3	2.0193E-03	5.6
Zircon 7, spot 1	2.0186E-03	5.2
Zircon 7, spot 2	2.0182E-03	5.0
Zircon 7, spot 3	2.0188E-03	5.3
Zircon 9, spot 1	2.0184E-03	5.1
Zircon 9, spot 2	2.0180E-03	4.9
Zircon 6, spot 1	2.0167E-03	4.3
Zircon 6, spot 2	2.0166E-03	4.2
KIM-5	2.0187E-03	–
KIM-5	2.0182E-03	–
KIM-5	2.0187E-03	–
KIM-5	2.0188E-03	–
KIM-5	2.0187E-03	–
KIM-5	2.0181E-03	–
KIM-5 avg	2.0184E-03	–
KIM-5 std dev (2σ)	1.0019E-06	0.5‰

Serpentinite: 153-920B-5R-1, 59–64 cm

Analysis	$^{18}O/^{16}O_{(meas)}$	$\delta^{18}O$ (VSMOW)
KIM-5	2.0164E-03	–
KIM-5	2.0160E-03	–
KIM-5	2.0152E-03	–
KIM-5	2.0155E-03	–
KIM-5	2.0155E-03	–
KIM-5	2.0163E-03	–
KIM-5	2.0154E-03	–
Zircon 1, spot 1	2.0185E-03	6.2
Zircon 1, spot 2	2.0172E-03	5.5
Zircon 1, spot 3	2.0164E-03	5.1
Zircon 1, spot 4	2.0181E-03	6.0
Zircon 1, spot 5	2.0162E-03	5.1
KIM-5	2.0161E-03	–
KIM-5	2.0155E-03	–
Zircon 2, spot 1	2.0168E-03	5.3
Zircon 2, spot 2	2.0171E-03	5.5
Zircon 2, spot 3	2.0175E-03	5.7
Zircon 2, spot 4	2.0162E-03	5.1
Zircon 2, spot 5	2.0167E-03	5.3
Zircon 2, spot 6	2.0178E-03	5.8
Zircon 1, spot 6	2.0182E-03	6.1
Zircon 1, spot 7	2.0175E-03	5.7
KIM-5	2.0165E-03	–
KIM-5	2.0169E-03	–
KIM-5	2.0166E-03	–
KIM-5	2.0163E-03	–
KIM-5	2.0167E-03	–
KIM-5	2.0165E-03	–
KIM-5	2.0165E-03	–
KIM-5	2.0165E-03	–
Zircon 4, spot 1	2.0172E-03	5.5
Zircon 4, spot 2	2.0169E-03	5.4
Zircon 4, spot 3	2.0165E-03	5.2
KIM-5	2.0170E-03	–
KIM-5	2.0167E-03	–
KIM-5	2.0167E-03	–
KIM-5	2.0170E-03	–
KIM-5 avg	2.0163E-03	–
KIM-5 std dev (2σ)	1.0943E-06	0.5‰

Discussion

Hydrothermal zircon

Although the zircon grains analyzed in this study preserve characteristics ($\delta^{18}O$, REE, Ti, growth zoning) typical of igneous zircon from primitive magmas (Valley et al. 2005), many of the host rocks are pervasively altered. To evaluate the possibility that the Leg 153 zircon samples are not magmatic, and may have precipitated from, or been altered by, hydrothermal fluids, the oxygen-isotope systematics between zircon and hydrothermal fluid (i.e., hot evolved seawater) were evaluated.

To estimate the $\delta^{18}O$ composition of the hydrothermal fluids involved in serpentinization at Leg 153, eight analyses of four Leg 153 serpentinite samples were made by laser fluorination and yield $\delta^{18}O$ (whole rock) values of 2.9 to 3.6‰ (Table 3). These serpentinites would have been in equilibrium with an aqueous fluid with $\delta^{18}O$ (H_2O) = –1.1 to 4.8‰ from 150 to 400 °C (Wenner and Taylor 1971). This predicted range is in excellent agreement with the measured range of $\delta^{18}O$ (H_2O) = 1.2 to 2.4‰ for hydrothermal fluids from several locations along the Mid-Atlantic Ridge, including near the Leg 153 site (Campbell et al. 1988; Jean-Baptiste et al. 1997). Thus assuming a hydrothermal fluid composition of $\delta^{18}O$ (H_2O) = 1.2 to 2.4‰ based on measured values appears to be geologically reasonable.

Equilibrium fractionation factors for $\Delta^{18}O$ (zircon-H_2O) were calculated from $\Delta^{18}O$ (quartz-zircon) (Valley et al. 2003) and $\Delta^{18}O$ (quartz-H_2O) (Clayton et al. 1972; Matsuhisa et al. 1979). Calculated equilibrium values for $\delta^{18}O$ (zircon) in equilibrium with $\delta^{18}O$ (H_2O) = 2.4‰ (i.e., MARK fluids), range from 0.2 to 0.7‰ over the temperature interval of 500 to 800 °C and decrease to values of $\delta^{18}O$ (zircon) = 0.2 to –4.4‰ at temperatures below 500 °C (Fig. 4). Decreasing the value of $\delta^{18}O$ (H_2O) from 2.4 to 0.0‰ (i.e., typical seawater) results in even lower values of $\delta^{18}O$ (zircon). An isotope salt effect (e.g., Horita et al. 1995) may

TABLE 2. Trace element abundances of Leg 153 zircon grains

Sample	153-920B-2R-1, 44-50 cm			153-922B-2R-2, 20-23 cm (mount "a")			
	grain 1	grain 3	grain 7	grain 1 core	grain 1 rim	grain 2	grain 3
CL pattern	osc, sec	osc, sec	osc, sec	osc, sec	osc, sec	sec	sec
$\delta^{18}O$ (‰)†	5.4	5.3	5.2	5.0	5.0	5.4	5.5
Ti	18.1	37	19.0	23.6	23.1	33.0	28.7
Y	1230	2120	2150	800	1230	920	800
Hf	7700	7300	7500	7800	7500	7700	7600
La	0.014	0.014	0.006	0.008	0.083	0.024	0.003
Ce	2.70	2.82	2.86	2.04	5.0	3.3	2.42
Pr	0.038	0.176	0.103	0.021	0.089	0.060	0.043
Nd	0.7	3.7	2.91	0.40	0.78	0.94	0.45
Sm	2.3	8.0	7.6	1.36	2.4	1.54	1.34
Eu	0.75	2.52	2.32	0.56	0.85	0.60	0.52
Gd	17.6	40	39.8	10.6	15.4	12.6	9.4
Tb	7.2	15.5	15.6	4.4	6.8	5.2	4.3
Dy	93	186	183	59	93	69	61
Ho	38.3	69	68	24.8	37.2	28.2	24.4
Er	177	288	299	114	178	132	116
Tm	38.7	59	61	25.7	38.0	29.4	25.5
Yb	366	520	530	236	337	270	239
Lu	70	96	96	49	70	55	49
Y/Ho	32	31	31	31	33	33	33
Σ REE	813	1288	1305	529	784	656	1135
$(Sm/La)_N$‡	300	940	2000	300	46	100	700
$(Ho/Gd)_N$	7.9	6.2	6.3	8.5	8.8	8.2	9.4
$(Yb/Sm)_N$	145	59	64	159	128	162	164
Ce/Ce*	28	14	27	39	14	21	52
Eu/Eu*	0.36	0.43	0.41	0.45	0.43	0.42	0.44
Ti *T* (°C)§	796	870	801	822	820	858	843

Notes: osc = oscillatory, sec = sector. Trace element abundance in ppm.
† Grain average. Per mil values are vs. VSMOW.
‡ "N" indicates a value normalized to the chondrite abundances of McDonough and Sun (1995).
§ Uncorrected Ti-in-zircon saturation thermometer of Watson and Harrison (2005).

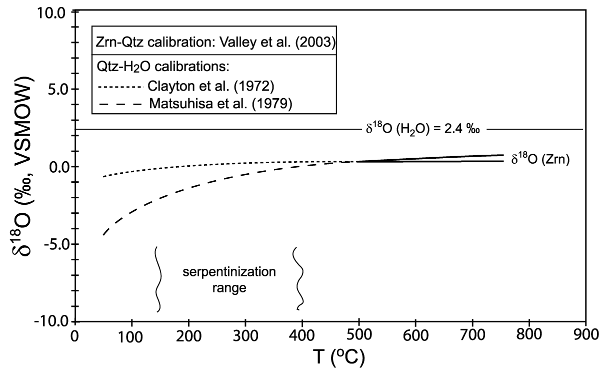


FIGURE 4. Calculated oxygen-isotope ratio for zircon in equilibrium with MARK hydrothermal fluids. Horizontal line labeled $\delta^{18}O$ (H_2O) indicates highest values measured for hydrothermal fluids at the MARK area (2.4‰, see text). Solid curves for $\delta^{18}O$ (zircon) indicate the temperature range of calibrations; dashed lines are extrapolated. Over the entire temperature range, the calculated fractionation between $\delta^{18}O$ (H_2O) and $\delta^{18}O$ (zircon) is positive. The highest calculated value of $\delta^{18}O$ (zircon) in equilibrium with MARK fluids at any temperature is 0.2‰.

TABLE 3. Leg 153 serpentinite whole-rock $\delta^{18}O$ values by laser fluorination (in ‰ vs. VSMOW)

Site	Hole	Core	Sect.	Interval (cm)	Rock type	$\delta^{18}O$	2 st. dev. (‰)
920	B	2R	1	44–50	serp. harz.	2.88 (n = 3)	0.04
920	B	5R	1W	59–64	serp. harz.	3.30 (n = 3)	0.14
920	D	2R	1	70–75	serp. harz.	3.56	0.14
920	D	2R	1W	126–132	serp. harz.	3.05	0.06

Notes: sect. = section, serp. = serpentinized, harz. = harzburgite; st. dev. = standard deviation = reproducibility of UWG-2. For samples with multiple analyses, the st. dev. is the reproducibility of duplicate analyses.

affect the $\delta^{18}O$ fractionation for zircon-water, however such an effect would be small (sub per mil) for MARK fluids with ~3.0 wt% NaCl (Campbell et al. 1988), relative to the large (>5‰) difference between $\delta^{18}O$ of calculated hydrothermal zircon and the measured MARK zircon samples. We conclude that the Leg 153 zircon samples measured in this study with $\delta^{18}O$ (zircon) = 5.3‰ could only have precipitated from a hydrous fluid if $\delta^{18}O$ (H_2O) was greater than 7‰, regardless of temperature, and thus these zircon grains could not have precipitated from known hydrothermal fluids in the MARK area. A magmatic origin in a mantle-derived melt uncontaminated by crustal material is thus consistent with the textural occurrence, $\delta^{18}O$ systematics, REE abundance, Ti temperatures, and the presence of igneous growth zoning preserved in many of these grains.

Eclogite zircon

The zircon-bearing samples from Leg 153 provide analogues for protoliths of modern and ancient zircon-bearing eclogites. Zircon is often found in remnants of subducted oceanic crust that has recrystallized to eclogite at depths >30 km prior to being exhumed back to the surface. The origin and significance of zircon in eclogite is debated, particularly for distinguishing igneous from metamorphic histories in geochronology studies. However, eclogites from Greece (Tomaschek et al. 2003; Bröcker and Keasling 2006), New Caledonia (Spandler et al. 2004), and Spain (Puga et al. 2005) contain zircon grains that preserve growth zoning, consistent with the Leg 153 zircon samples as having an origin during the igneous construction of the oceanic crust. In addition, the apparent stability of zircon in these samples provides insight into the mobility of U, Th, Zr, and Hf for geochemical modeling of the cycling of these elements between the crust and mantle during subduction (e.g., Pfander et al. 2007).

Early-Archean detrital zircon

Documenting a mantle signature of $\delta^{18}O$ in mid-ocean ridge zircon also provides an important framework for interpreting $\delta^{18}O$ values in zircon from unknown protoliths (e.g., detrital or xenocrystic grains). One important application is in early Earth studies, and the origin of "mildly elevated" $\delta^{18}O$ values in detrital zircon grains that pre-date the preserved rock record. Values of $\delta^{18}O$ (zircon) from 6.3 to 7.5‰ in >3900 million-year-old detrital zircon are among the strongest lines of evidence for the existence of granitic continent-like crust and liquid water oceans (e.g., a hydrosphere) during the first 500 Ma years of Earth history (Cavosie et al. 2007), with the rationale that the melting of high $\delta^{18}O$ crust previously altered at low temperatures by water (e.g., <200 °C) is required to produce zircon with elevated $\delta^{18}O$ values relative to the mantle (Valley et al. 2002). Implicit in this argument is that high $\delta^{18}O$ zircon (e.g., >6.3‰) could not have been produced in uncontaminated mantle-derived melts because low-temperature conditions are

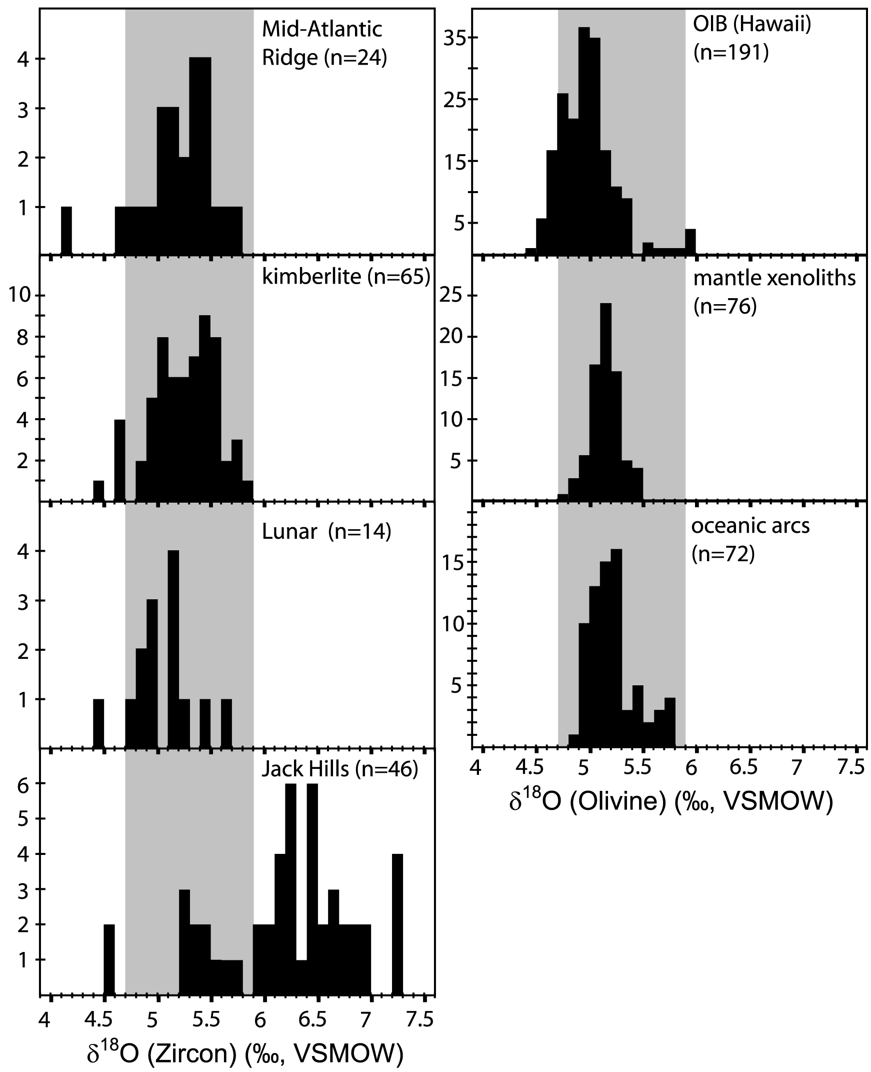


FIGURE 5. Histogram of $\delta^{18}O$ values for zircon and olivine. Zircon data: Mid-Atlantic Ridge (this study), kimberlite (Valley et al. 1998; Page et al. 2007), Lunar (Nemchin et al. 2006), Jack Hills (Mojzsis et al. 2001; Peck et al. 2001; Cavosie et al. 2005). Olivine data: OIB (Eiler et al. 1996, 2000; Wang et al. 2003), mantle xenoliths (Mattey et al. 1994), oceanic arcs (Eiler et al. 2000). The shaded field at $\delta^{18}O$ = 4.7 to 5.9‰ encompasses primitive mantle values of $\delta^{18}O$ (zircon) = 5.3 ± 0.6‰ (Page et al. 2007; Valley et al. 1998). All olivine data are by laser fluorination. $\Delta^{18}O$ (Zrc-Ol) = 0.2 ‰ at magmatic temperatures.

necessary to create fractionated source reservoirs capable of crystallizing high $\delta^{18}O$ zircon when melted. The $\delta^{18}O$ values for the Leg 153 zircon samples have the same narrow range of primitive values as zircon grains from kimberlite, the Moon, and olivine from a variety of mantle-derived rocks (Fig. 5). These results support prior conclusions that $\delta^{18}O$ values higher than ~6.3‰ in igneous zircon are not found in mantle-derived igneous rocks, and require a component of crust altered at low temperatures. In the case of the high-$\delta^{18}O$ Jack Hills zircon grains, the oxygen-isotope ratios demonstrate that many of the >3900 Ma zircon grains could not have been produced in a tectonic setting analogous to the Mid-Atlantic Ridge (Cavosie et al. 2007; Grimes et al. 2007), thus requiring other tectonic regimes to have been active on the Early Earth.

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