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ORIGINAL PAPER

The origin of high $\delta^{18}O$ zircons: marbles, megacrysts, and metamorphism

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Abstract The oxygen isotope ratios ($\delta^{18}O$) of most igneous zircons range from 5 to 8‰, with 99% of published values from 1345 rocks below 10‰. Metamorphic zircons from quartzite, metapelite, metabasite, and eclogite record $\delta^{18}O$ values from 5 to 17‰, with 99% below 15‰. However, zircons with anomalously high $\delta^{18}O$, up to 23‰, have been reported in detrital suites; source rocks for these unusual zircons have not been identified. We report data for zircons from Sri Lanka and Myanmar that constrain a metamorphic petrogenesis for anomalously high $\delta^{18}O$ in zircon. A suite of 28 large detrital zircon megacrysts from Mogok (Myanmar) analyzed by laser fluorination yields $\delta^{18}O$ from 9.4 to 25.5‰. The U–Pb standard, CZ3, a large detrital zircon megacryst from Sri Lanka, yields $\delta^{18}O = 15.4 \pm 0.1$‰ (2 SE) by ion microprobe. A euhedral unzoned zircon in a thin section of Sri Lanka granulite facies calcite marble yields $\delta^{18}O = 19.4$‰ by ion microprobe and confirms a metamorphic petrogenesis of zircon in marble. Small oxygen isotope fractionations between zircon and most minerals require a high $\delta^{18}O$ source for the high $\delta^{18}O$ zircons. Predicted equilibrium values of $\Delta^{18}O$(calcite-zircon) = 2–3‰ from 800 to 600°C show that metamorphic zircon crystallizing in a high $\delta^{18}O$ marble will have high $\delta^{18}O$. The high $\delta^{18}O$ zircons (>15‰) from both Sri Lanka and Mogok overlap the values of primary marine carbonates, and marbles are known detrital gemstone sources in both localities. The high $\delta^{18}O$ zircons are thus metamorphic; the 15–25‰ zircon values are consistent with a marble origin in a rock-dominated system (i.e., low $\text{fluid}_{(\text{external})}$/rock); the lower $\delta^{18}O$ zircon values (9–15‰) are consistent with an origin in an external fluid-dominated system, such as skarn derived from marble, although many non-metasomatized marbles also fall in this range of $\delta^{18}O$. High $\delta^{18}O$ (>15‰) and the absence of zoning can thus be used as a tracer to identify a marble source for high $\delta^{18}O$ detrital zircons; this recognition can aid provenance studies in complex metamorphic terranes where age determinations alone may not allow discrimination of coeval source rocks. Metamorphic zircon megacrysts have not been reported previously and appear to be associated with high-grade marble. Identification of high $\delta^{18}O$ zircons can also aid geochronology studies that seek to date high-grade metamorphic events due to the ability to distinguish metamorphic from detrital zircons in marble.

Keywords Zircon · Oxygen isotopes · Sri Lanka · Mogok · Marble · Megacryst · SIMS

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Introduction

The widespread occurrence and durability of zircon in many geologic environments have resulted in the development of an array of different chemical and isotopic

analytical methods to understand its petrogenesis. Zircon has been shown to be highly retentive of oxygen isotope ratio (δ^{18}O) over a wide range of geologic conditions and time (Valley et al. 1994; Watson and Cherniak 1997; Peck et al. 2003; Page et al. 2007a; Moser et al. 2008). With accurate empirical and theoretical oxygen isotope fractionation factors for zircon and co-existing phases (Valley 2003), analysis of δ^{18}O in zircon offers unique insights into a variety of petrologic processes, including the recognition of primitive mantle-equilibrated melts (Valley et al. 1998; Page et al. 2007b; Cavosie et al. 2009; Grimes et al. 2011), evidence of the first continents and oceans (Wilde et al. 2001; Cavosie et al. 2005); evolution of the continental crust (Valley et al. 2005; Hawkesworth and Kemp 2006; Moser et al. 2008); origin of large batholiths (Lackey et al. 2005, 2008); origin of low δ^{18}O magmas (Bindeman and Valley 2001; Bindeman et al. 2008), evaluation of mineral-melt and mineral–mineral equilibria (King et al. 2001; Valley et al., 2003; Lackey et al. 2006; Trail et al. 2009), and a monitor of whole-rock alteration (King et al. 1997). Studies of δ^{18}O in metamorphic zircon also yield important information about sub-solidus processes, including the composition of crustal fluids, partial melting, and recrystallization (Peck et al. 2003; Martin et al. 2006; Page et al. 2007a; Lancaster et al. 2009; Gordon et al. 2009). In addition to "normal" igneous and metamorphic zircon, there exist lesser-known occurrences of anomalously high δ^{18}O zircons, with δ^{18}O values higher than values reported in zircon from common igneous and pelitic/siliceous metamorphic rocks (e.g., >15‰). Determining the origin of such high δ^{18}O in zircon is the focus of this paper.

Here, we present laser fluorination analyses of δ^{18}O for a population of detrital zircons from Mogok (Myanmar) and ion microprobe measurements of δ^{18}O for two zircons from Sri Lanka. One of the Sri Lanka zircons is the widely used U–Pb standard CZ3, and the other is a zircon from a granulite facies marble. In conjunction with previous work, the new δ^{18}O data allow the first robust constraints to be placed on the origin of high δ^{18}O zircons. Of significance to the question of origin is the surprising fact that all reported occurrences of high δ^{18}O zircons ($\delta^{18}O > 15‰$) are either detrital or from an unusual source where reliable determinations of protolith have not been possible. A better understanding of origin based on oxygen isotope systematics will allow the high δ^{18}O values recorded in these grains to be used as a tracer for investigating the metamorphic petrogenesis of zircon.

The δ^{18}O of igneous zircon

Nearly all δ^{18}O studies of zircon (Zrn) have focused on magmatic grains, resulting in the recognition that most igneous zircon is either in high temperature equilibrium with mantle oxygen isotope ratios (δ^{18}O(Zrn) = 5.3 ± 0.6‰) or slightly higher (see reviews by Valley 2003; Valley et al. 2005). The upper limit for igneous δ^{18}O(Zrn) has increased from primitive mantle values of ~5–6‰ to evolved values of ~10‰ since the end of the Archean as a consequence of tectonics, changes in the atmosphere, evolving processes of weathering, and maturation of the crust (Valley et al. 2005). However, 99% of the reported δ^{18}O values for igneous zircon of all ages are below 10‰ (Fig. 1a). One notable exception is a suite of rare high δ^{18}O granitic rocks in the Grenville Frontenac Terrane (Shieh 1985), where granitoids are interpreted to have originated from melting of buried pelitic sediments and yield zircons with δ^{18}O up to 13.5‰ (Peck et al. 2004). Given that no other granitoids of any age have been found with such high δ^{18}O(Zrn) (Valley et al. 2005), the anomalously high δ^{18}O Frontenac zircons are considered unique. Igneous zircons can thus be characterized as having $\delta^{18}O < 10‰$.

The δ^{18}O of metamorphic zircon

We use the term "metamorphic zircon" to refer to whole zircons or parts of grains (e.g., rims) whose δ^{18}O

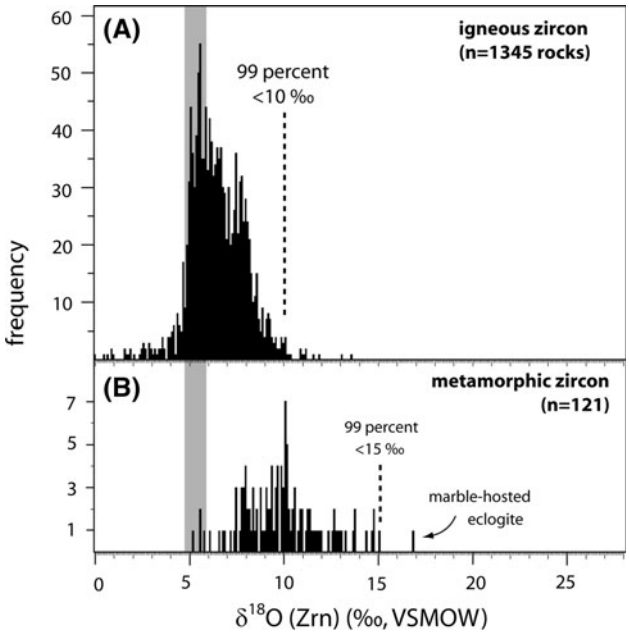

Fig. 1 Compilation of oxygen isotope ratios for zircon from igneous and metamorphic rocks. The *shaded vertical bar* indicates range of mantle-equilibrated zircon, 5.3 ± 0.6‰ (2 sd, Valley et al. 2005). **a** Oxygen isotope data for zircons separated from 1345 igneous rocks. Note that 99% of all igneous data are lower than 10‰ (*dashed vertical line*). **b** Oxygen isotope data for metamorphic zircons and rims from quartzites, metapelites, and metabasites. Note that 99% of all metamorphic data are lower than 15‰ (*dashed vertical line*). Data in **a** are from Valley et al. 2005 (n = 1,117) and 15 additional studies published from 2006–2010 (n = 228); references in Online Resource 1)

composition results from sub-solidus processes, such as recrystallization or other processes that record oxygen isotope exchange with the host rock or fluids. Most published $\delta^{18}O$ data for metamorphic zircon (99%) range from 5 to 15‰ (average = 9.8‰) and are from metapelites and quartzites from the Adirondack Mountains (USA) and the Kapuskasing uplift (Canada), and metapelites and metabasites from Naxos (Greece) (Fig. 1b). Ion microprobe studies have demonstrated that zircon rims from Adirondack granulites (quartzites and pelitic migmatites) yield $\delta^{18}O$ as high as 12.8‰ (Peck et al. 2003; Page et al. 2007a; Lancaster et al. 2009); zircon rims from Adirondack amphibolite facies rocks (pelitic migmatites) yield similar values up to 13.2‰ (Lancaster et al. 2009). The upper value of ~13‰ for Adirondack metamorphic zircon is thus comparable to that found in igneous zircon from the Frontenac granitoids, which is higher than all other igneous zircons. Detrital zircons from granulite facies quartzites in the Kapuskasing uplift contain igneous cores surrounded by metamorphic rims that yield $\delta^{18}O$ from 8.4 to 10.4‰ (Moser et al. 2008). At Naxos, metamorphic rims on zircons from metapelitic gneiss yield $\delta^{18}O$ up to 15‰ as measured by ion microprobe and represent the highest $\delta^{18}O$ values published for zircons from metapelitic rocks (Martin et al. 2006).

High $\delta^{18}O$ zircons

Three occurrences of zircon with high $\delta^{18}O$ values from unknown or obscure source rocks have been published. Peck et al. (2001) and Valley (2003) report a $\delta^{18}O$ value of 22.9‰ for "Mog" (USNM #R18113), a large detrital zircon from a placer deposit in an amphibolite terrane near Mogok, Myanmar. The Mogok area is known for the mining of placer deposits that yield large gemstones such as corundum, forsterite, and spinel (Yui et al. 2008). Nasdala et al. (2008) reported a $\delta^{18}O$ of 13.9‰ for M257, a zircon U–Pb standard from Sri Lanka. Zircon M257 is a large megacryst (long dimension = 20 mm) detrital zircon from a placer deposit in the Highlands Southwest Complex, a granulite terrane in Sri Lanka that is also known for the mining of gemstones from placer deposits (Nasdala et al. 2008). Like Mog, the protolith of M257 is not known. The only report of an anomalously high $\delta^{18}O$ zircon from a known source rock is from an ultra-high pressure (UHP) terrane in the Dabie-Sulu Orogen, China. Zircons separated from an eclogite facies boudin of metasedimentary rock hosted in a UHP marble yield $\delta^{18}O = 16.8‰$ by bulk laser analysis (Wu et al. 2006a). The authors cite the high $\delta^{18}O$ as evidence that oxygen isotope equilibrium was attained between the eclogite protolith and the zircons and was buffered by the high $\delta^{18}O$ marble. Wu et al. (2006a) reported that cathodoluminescence (CL) imaging and U–Pb spot analysis showed that many of the zircons contain inherited cores with two distinct overgrowths; thus the bulk analysis of $\delta^{18}O = 16.8‰$ is an average of core and multiple rim domains.

Samples and methods

Detrital zircons (Myanmar)

Twenty-eight detrital zircons from a fluvial deposit near Mogok (Myanmar) were analyzed for $\delta^{18}O$ in this study. The zircons are rounded, large (2–8 mm in length), and occur in a variety of colors, including dark red, orange, olive green, yellow, and clear (see color images in Online Resource 2). The Mogok zircons were analyzed for $\delta^{18}O$ in ~2 mg aliquots at the University of Wisconsin by gas source mass spectrometry using BrF_5 and a 32 W CO_2 laser. Sample analyses were corrected for accuracy with UWG-2 garnet ($\delta^{18}O = 5.8‰$ VSMOW) (Valley et al. 1995) analyzed multiple times at the beginning of the run. The reproducibility of UWG-2 for the two analytical sessions (May 5, 2008 and May 6, 2009) was 0.04‰ (2 standard deviations, SD) for each session.

U–Pb standard CZ3 (Sri Lanka)

CZ3 is a zircon U–Pb standard from a fluvial deposit in a granulite terrane from Sri Lanka (Pidgeon et al. 1994). The CZ3 crystal was a large ~1 g zircon with no observable zoning (Pidgeon et al. 1994) and was adopted as the primary U–Pb standard used at the Curtin University SHRIMP facility (Nelson 1997; de Laeter and Kennedy 1998). CZ3 has a $^{206}Pb/^{238}U$ age of 564 Ma, and U and Th concentrations of 551 ± 10 ppm and 30 ± 2, respectively (Pidgeon et al. 1994; Nelson 1997; Nasdala et al. 2004). Forty analyses of rare earth elements (REE) by SHRIMP-RG yield an average ΣREE abundance of 26 ppm (Mattinson et al. 2006). The Lu–Hf isotope compositions of CZ3 are $^{176}Lu/^{177}Hf = 0.000034$ and $^{176}Hf/^{177}Hf = 0.281729$ (Xu et al. 2004; Wu et al. 2006b), which yield $\varepsilon Hf_{(564)} = -25.5$ (Xu et al. 2004).

Six chips of CZ3 were analyzed for $\delta^{18}O$ by ion microprobe. The chips were previously embedded in four 25-mm-diameter epoxy mounts where they were utilized as U–Pb standards (Cavosie et al. 2004). Cathodoluminescence (CL) imaging of the six chips yields mostly homogeneous images showing contrast variations only around cracks. No growth zoning (magmatic or otherwise) or mineral inclusions were observed in any chips of CZ3, consistent with previous descriptions (Pidgeon et al. 1994; Nasdala et al. 2004). The mounts were re-polished to remove pits following U–Pb determinations and analyses for $\delta^{18}O$ were performed using a CAMECA IMS-1280 ion

microprobe at the University of Wisconsin from July 19–21, 2006.

Zircon-bearing marble CJJ4 (Sri Lanka)

A zircon identified in a thin section of a granulite facies marble from Sri Lanka was analyzed for $\delta^{18}O$ by ion microprobe. Rock sample CJJ4 was collected by Elsenheimer (1988) from the Highlands Southwest Complex of Sri Lanka and reported to contain 70% carbonate. Elsenheimer (1988) reported the assemblage calcite + diopside + phlogopite + pyrite + scapolite + titanite + tremolite + zircon and a value for $\delta^{18}O$(calcite) of 23.6‰. In an archived thin section (UW #1845-88) cut from sample CJJ4, a euhedral zircon was identified enclosed in a calcite + tremolite matrix (Fig. 2a) and is interpreted on textural considerations to be a metamorphic zircon. No discernable cathodoluminescence signal was detected from this zircon (see image in Online Resource 3).

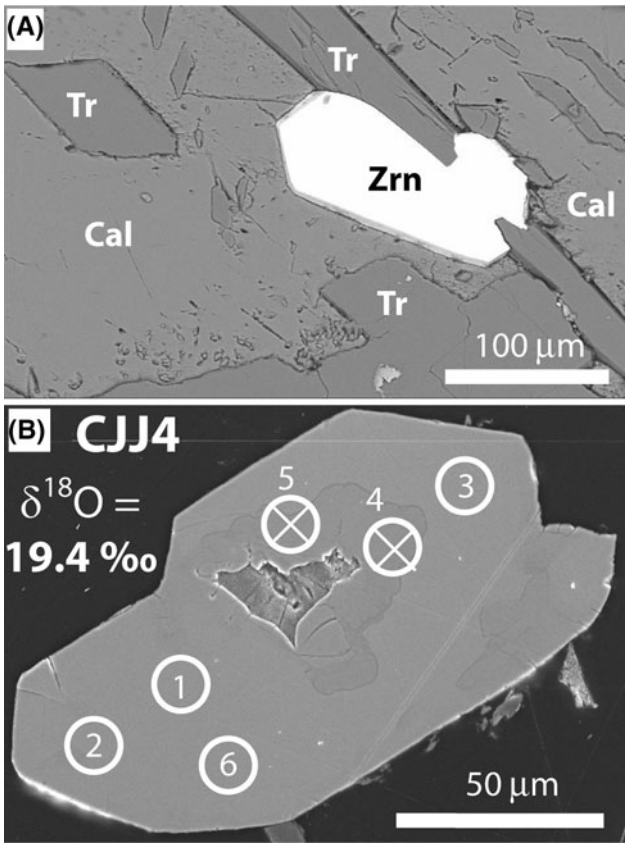

Fig. 2 Zircon CJJ4 from Sri Lanka granulite facies marble. **a** Back-scattered electron image of zircon CJJ4 in thin section, prior to removal for casting in epoxy. **b** Secondary electron image of zircon CJJ4 after casting in epoxy and re-polishing. The *lower-left tip* of the zircon correlates with the tip on the *left side* of the zircon in **a**. White circles indicate location of $\delta^{18}O$ analysis pits by ion microprobe, including analysis number (Table 2). *Zrn* zircon; *Tr* tremolite; *Cal* calcite

The zircon was cast in the center of a 25-mm epoxy mount and re-polished (Fig. 2b), along with a chip of zircon oxygen isotope standard KIM5 for $\delta^{18}O$ analysis by ion microprobe.

WiscSIMS Cameca 1280 ion microprobe methods

Analysis protocols for $\delta^{18}O$ in zircon closely follow those described elsewhere (Kita et al. 2009; Valley and Kita 2009). A $^{133}Cs^{+}$ primary ion beam (20 keV total impact voltage) was focused to a diameter of 10 µm on the sample surface. Secondary O^{-} ions were accelerated from the sample by −10 kV, and the analysis site was centered under a uniform electron field generated by a normal-incidence electron gun for charge compensation. The intensity of ^{16}O was $\sim 2 \times 10^9$ cps, depending on the primary intensity (ca. 1×10^9 cps/nA). Mass resolving power was set to ca. 2,500, sufficient to separate hydride interferences on ^{18}O. Two multi-collector Faraday cups (FC) were used for simultaneous measurement of ^{16}O and ^{18}O. The base line of the FC amplifiers was calibrated at the beginning of each analytical session. Total analytical time per spot was about 4 min, including time for locating and selecting the analytical positions (1–2 min), pre-sputtering (10 s), automatic retuning of the secondary beam (ca. 60 s), and analysis (80 s). Chips of zircon standard KIM-5 ($\delta^{18}O = 5.09 \pm 0.12$‰, 2 SD (standard deviation) VSMOW, Valley 2003; Cavosie et al. 2005) embedded in the sample mounts were used to calibrate $\delta^{18}O$ analyses of CZ3 and CJJ4.

Results

Sixteen $\delta^{18}O$ analyses were performed on Sri Lanka zircon CZ3 by ion microprobe and calibrated with 40 bracketing analyses of KIM-5 (Table 1). The average of all CZ3 analyses made on the six grains in four different analytical sessions over 3 days (July 19–21, 2006) is $\delta^{18}O = 15.43 \pm 0.42$‰ VSMOW (2 SD, $n = 16$, 2 standard error = 0.10‰) (Fig. 3). Uncertainty listed for individual analyses is based on the reproducibility of KIM-5 during that session and ranges from 0.32 to 0.39‰ (2 SD). The SD of all 16 measurements of CZ3 (±0.42‰, 2 SD) is only slightly larger than that for KIM-5 in any given session (Table 1).

Six analyses of $\delta^{18}O$ were performed on zircon CJJ4 by ion microprobe and calibrated with 12 bracketing analyses of KIM-5 (Table 2). During post-$\delta^{18}O$ analysis imaging of the analytical pits, analyses #4 and #5 were found to have been made close to a ~40-µm hole in the center of the grain that may have resulted from the preferential removal of intergrown calcite during polishing (Fig. 2a). The two

Table 1 Cameca 1280 oxygen isotope analyses of zircon U–Pb standard CZ3

Grain-spot	$^{18}O/^{16}O$ (meas, $\times 10^3$)	2 SE	$\delta^{18}O$ (meas)	2 SE	$\delta^{18}O$ (VSMOW)	2 SD
Mount 01JH-13b (chip 1) July 19, 2006						
KIM5-44	2.01837	0.00041	6.57	0.20		
KIM5-45	2.01742	0.00043	6.09	0.21		
KIM5-46	2.01766	0.00062	6.21	0.31		
KIM5-47	2.01806	0.00046	6.42	0.23		
KIM5-48	2.01770	0.00056	6.23	0.28		
KIM5-49	2.01796	0.00040	6.36	0.20		
CZ3-1.1	2.03817	0.00051	16.44	0.25	15.21	0.32
CZ3-1.2	2.03924	0.00043	16.97	0.21	15.74	0.32
CZ3-1.3	2.03880	0.00059	16.76	0.29	15.52	0.32
KIM5-50	2.01732	0.00062	6.04	0.31		
KIM5-51	2.01787	0.00047	6.32	0.23		
KIM5-52	2.01823	0.00055	6.50	0.27		
KIM5-53	2.01822	0.00054	6.49	0.27		
KIM5-54	2.01784	0.00054	6.31	0.27		
KIM5-55	2.01799	0.00058	6.38	0.29		
KIM-5 ($n = 12$)						0.32
Mount 01JH-36 (chip 2) July 20, 2006						
KIM5-1	2.01774	0.00061	6.26	0.30		
KIM5-2	2.01865	0.00057	6.71	0.28		
KIM5-3	2.01856	0.00051	6.67	0.25		
KIM5-4	2.01844	0.00054	6.60	0.27		
KIM5-5	2.01899	0.00043	6.88	0.22		
KIM5-6	2.01834	0.00046	6.55	0.23		
CZ3-2.1	2.03876	0.00037	16.74	0.18	15.25	0.32
KIM5-7	2.01838	0.00047	6.57	0.23		
KIM5-8	2.01819	0.00054	6.48	0.27		
KIM5-9	2.01836	0.00050	6.57	0.25		
KIM5-10	2.01826	0.00057	6.52	0.28		
KIM-5 ($n = 10$)						0.32
Mount 01JH-54b (chip 3) July 21, 2006						
KIM5-11	2.01867	0.00055	6.72	0.27		
KIM5-12	2.01886	0.00052	6.81	0.26		
KIM5-13	2.01912	0.00042	6.94	0.21		
KIM5-14	2.01838	0.00056	6.57	0.28		
CZ3-3.1	2.03977	0.00053	17.24	0.26	15.55	0.33
CZ3-3.2	2.03938	0.00048	17.04	0.23	15.35	0.33
CZ3-3.3	2.04011	0.00031	17.41	0.15	15.72	0.33
KIM5-15	2.01932	0.00049	7.04	0.24		
KIM5-16	2.01879	0.00045	6.78	0.22		
KIM5-17	2.01912	0.00042	6.94	0.21		
KIM5-18	2.01844	0.00050	6.60	0.25		
KIM5-19	2.01850	0.00046	6.63	0.23		
KIM-5 ($n = 9$)						0.33
Mount W74/4 (chip 4, 5, 6) July 21, 2006						
KIM5-1	2.01747	0.00050	6.12	0.25		
KIM5-2	2.01805	0.00042	6.41	0.21		
KIM5-3	2.01775	0.00057	6.26	0.28		

Table 1 continued

Grain-spot	$^{18}O/^{16}O$ (meas, $\times 10^3$)	2 SE	$\delta^{18}O$ (meas)	2 SE	$\delta^{18}O$ (VSMOW)	2 SD
KIM5-4	2.01792	0.00036	6.34	0.18		
CZ3-4.1	2.03880	0.00042	16.76	0.21	15.47	0.39
CZ3-5.1	2.03808	0.00033	16.40	0.16	15.12	0.39
CZ3-6.1	2.03899	0.00054	16.85	0.26	15.57	0.39
CZ3-4.2	2.03810	0.00052	16.41	0.25	15.12	0.39
CZ3-5.2	2.03814	0.00040	16.43	0.20	15.15	0.39
CZ3-6.2	2.03867	0.00047	16.69	0.23	15.41	0.39
CZ3-4.3	2.03870	0.00040	16.71	0.20	15.42	0.39
CZ3-5.3	2.03902	0.00045	16.87	0.22	15.58	0.39
CZ3-6.3	2.03921	0.00056	16.96	0.28	15.68	0.39
KIM5-5	2.01833	0.00044	6.55	0.22		
KIM5-6	2.01803	0.00049	6.40	0.24		
KIM5-7	2.01877	0.00038	6.77	0.19		
KIM5-8	2.01764	0.00038	6.20	0.19		
KIM5-9	2.01785	0.00050	6.31	0.25		
KIM-5 ($n = 9$)						0.39
CZ3 (average, $n = 16$)				0.11	15.43	0.42

Analyses are listed in chronological order, within each session

Sample analyses are bracketed by the zircon standard KIM-5

Meas measured, *SE* standard error, *SD* standard deviation

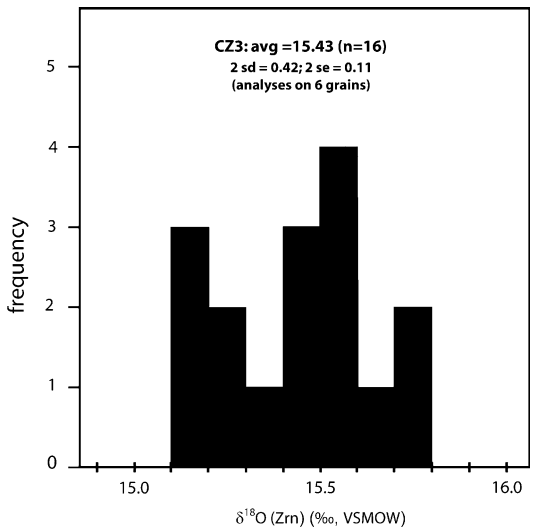

Fig. 3 Histogram of oxygen isotope analyses of zircon U–Pb standard CZ3 by ion microprobe

pits were located on rough surfaces of the zircon that were slightly lower than the polished surface and hence not made on a polished surface (Fig. 2b). Given the irregular nature of these pits, data from these two analyses were not considered further based on published criteria for the evaluation and rejection of irregular pits (Cavosie et al. 2005). The remaining four analyses yield $\delta^{18}O = 19.4 \pm 0.6‰$ (2 SD) VSMOW. Uncertainty listed for individual analyses is based on the reproducibility of KIM-5 during that session and ranges from 0.34 to 0.28‰ (2 SD). The $\delta^{18}O$ values for CZ3 and CJJ4 are plotted in Fig. 4a along with previously published data from Sri Lanka, including calcite from granulite facies marbles and corundum from skarns and detrital deposits. Also plotted in Fig. 4a is a shaded field indicating the range of $\delta^{18}O$(zircon) in equilibrium with measured $\delta^{18}O$(calcite) at 700°C.

Analyses for $\delta^{18}O$ were performed on 28 detrital zircons from Mogok by laser fluorination during analytical sessions on May 5, 2008, and May 6, 2009 (Table 3). The $\delta^{18}O$ values range from 9.37 to 25.48‰, with an average of 18.64‰. An uncertainty of 0.04‰ (2 SD) for individual analyses of Mogok zircons is based on the reproducibility of UWG-2 during the sessions. The $\delta^{18}O$ values for the Mogok zircons are plotted in Fig. 4b along with previously published data from Mogok, including calcite from amphibolite facies marbles and other minerals from marble and detrital deposits.

Discussion

Constraints on the source rocks of high $\delta^{18}O$ zircons

The large range in $\delta^{18}O$ for both the Sri Lanka and Mogok $\delta^{18}O$(Zrn) data sets (Fig. 4) requires multiple source rocks.

Table 2 Cameca 1280 oxygen isotope analyses of Sri Lanka zircon CJJ4

Grain-spot	$^{18}O/^{16}O$ (meas, $\times 10^3$)	2 SE	$\delta^{18}O$ (meas)	2 SE	$\delta^{18}O$ (VSMOW)	2 SD
Mount CJJ4: August 10, 2009						
KIM5-1	2.01717	0.00037	5.97	0.18	–	
KIM5-2	2.01764	0.00044	6.20	0.22	–	
KIM5-3	2.01740	0.00044	6.08	0.22	–	
KIM5-4	2.01716	0.00054	5.96	0.27	–	
CJJ4-1	2.04679	0.00038	20.74	0.19	19.66	0.34
KIM5-5	2.01748	0.00071	6.12	0.35	–	
KIM5-6	2.01821	0.00040	6.49	0.20	–	
KIM5-7	2.01781	0.00044	6.29	0.22	–	
KIM5-8	2.01760	0.00050	6.18	0.25	–	
CJJ4-2	2.04554	0.00043	20.12	0.21	18.94	0.28
CJJ4-3	2.04661	0.00035	20.65	0.17	19.47	0.28
CJJ4-4	2.02765	0.00037	11.20	0.18	10.02[a]	0.28
CJJ4-5	2.02950	0.00030	12.12	0.15	10.94[a]	0.28
CJJ4-6	2.04684	0.00045	20.77	0.22	19.58	0.28
KIM5-9	2.01791	0.00034	6.34	0.17	–	
KIM5-10	2.01739	0.00032	6.08	0.16	–	
KIM5-11	2.01760	0.00045	6.19	0.22	–	
KIM5-12	2.01798	0.00041	6.37	0.21	–	
CJJ4 (average, $n = 4$)					19.4	0.6

Analyses are listed in chronological order, within each session

Sample analyses are bracketed by the zircon standard KIM-5

Meas measured, *SE* standard error, *SD* standard deviation

[a] Irregular analysis spot- data rejected. See text for discussion

The high $\delta^{18}O$ values of the Sri Lanka (13.9–19.4‰) and Mogok (9.4–25.5‰) zircons allow first-order constraints to be placed on the nature of these sources. Crustal sources are indicated, as zircons with $\delta^{18}O > 6‰$ are not known from uncontaminated mantle-derived magmas (Valley et al. 1998; Cavosie et al. 2009; Grimes et al. 2011). A metamorphic origin is also indicated for the $\delta^{18}O$(Zrn) values >13.5‰ (27 of 32 grains, 84%), as igneous zircons with $\delta^{18}O$ above 13.5‰ are not known and values above 10‰ are rare (Valley et al. 2005) (Fig. 1a). Relatively small oxygen isotope fractionations between most minerals and zircon at high temperature (Valley 2003) further require the source rocks to have higher $\delta^{18}O$ (whole-rock) values than the zircons. Sedimentary rocks, such as shale, chert, limestone, as well as metamorphosed equivalents, have high primary $\delta^{18}O$ values relative to igneous rocks (e.g., >15‰) (Valley et al. 2005) and are thus suitable candidates for potential source rocks of the high $\delta^{18}O$ zircons. Pelitic shale can have whole-rock $\delta^{18}O$ up to 24‰; a global survey of shale yields an average $\delta^{18}O$ of 17‰ (Land and Lynch 1996). While shale is a high $\delta^{18}O$ source, metamorphosed shale does not appear to be a likely protolith for the large detrital zircons analyzed in this study, as zircons reported from metapelites are not megacrystic and commonly preserve growth zoning and inherited detrital cores (Dempster et al. 2004; Rasmussen 2005). The three high $\delta^{18}O$ Sri Lankan zircons (CJJ4, CZ3, and M257) all show an absence of growth zoning in CL. The highest values of $\delta^{18}O$ for metamorphic rims on Adirondack and Naxos zircons (up to 15‰) partially overlap 9 of 32 (30%) of the lowest $\delta^{18}O$ zircons from Sri Lanka and Mogok (Figs. 1, 4); however, the high $\delta^{18}O$ domains in the Adirondack and Naxos zircons occur as rims around clearly identifiable zoned cores, not as large unzoned megacrystic zircons.

Chert is a high $\delta^{18}O$ source rock, and zircon in oxygen isotope equilibrium with high $\delta^{18}O$ chert (SiO_2) is predicted to have similarly high $\delta^{18}O$ (Valley et al. 2003). Zircon occurrences in chert appear to be rare and may reflect the paucity of available Zr. The only $\delta^{18}O$ reported for zircon in metamorphosed chert is by Page et al. (2009), who reported metamorphic rims with $\delta^{18}O$ from 17 to 24‰ around zircons with oscillatory-zoned inherited igneous cores ($\delta^{18}O = 4.7$–$9.1‰$) in amphibolite facies chert on Santa Catalina Island (USA). The high $\delta^{18}O$ rims from the Santa Catalina metachert zircons overlap with the highest $\delta^{18}O$ zircons from both Sri Lanka and Mogok. However, similar to the metapelite zircons, the high $\delta^{18}O$ components

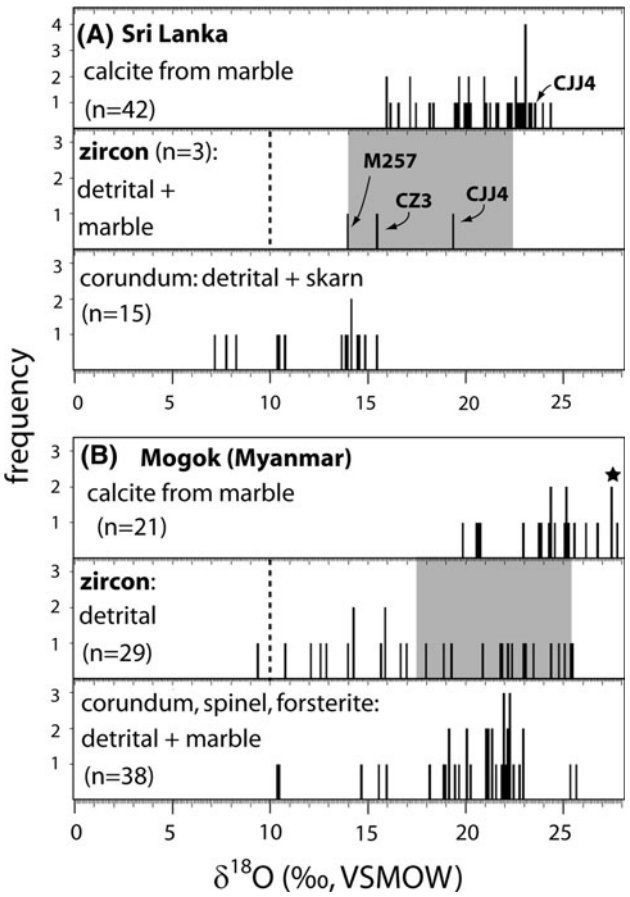

Fig. 4 Compilation of oxygen isotope ratios for zircon and other minerals from Sri Lanka and Mogok (Myanmar). **a** Sri Lanka data include $\delta^{18}O$ values of calcite from granulite facies marbles (Elsenheimer 1988; Hoffbauer and Spiering 1994); detrital zircon megacrysts CZ3 (this study) and M257 (Nasdala et al. 2008); zircon from granulite facies marble (CJJ4, this study); and corundum from various sources (Giuliani et al. 2005). **b** Mogok data include $\delta^{18}O$ values of calcite from amphibolite facies marbles (Garnier et al. 2008; Yui et al. 2008); detrital zircons (this study: $n = 28$; Valley 2003: $n = 1$); and corundum, spinel, and forsterite (Garnier et al. 2008; Giuliani et al. 2005; Yui et al. 2008). The star indicates the interpreted primary calcite $\delta^{18}O$ value of 27.5‰ by Yui et al. (2008). The vertical dashed line in both zircon histograms at 10‰ is the igneous "99% limit" indicated in Fig. 1a. The shaded area in both zircon histograms indicates the range of $\delta^{18}O$ values calculated for zircon in equilibrium with the measured range of $\delta^{18}O$ values for **a** Sri Lanka calcite at 800°C and **b** Mogok calcite at 700°C. Note that choosing lower metamorphic temperatures would shift the shaded ranges in both histograms to the *left*. See text for discussion

of the Santa Catalina zircons occur as rims around igneous cores, rather than as large megacrystic zircon, and no inherited cores or other growth zoning has been observed in the Sri Lanka zircons.

Marine carbonates, or marbles, commonly have $\delta^{18}O$(calcite) >17‰ (Valley 1986); values up to 28‰ have been reported for many greenschist to granulite facies marbles (Fig. 5). For this discussion, we use "marble" to describe calcite- or dolomite-rich rocks produced from the recrystallization of a marine carbonate protolith regardless of the extent of fluid–rock interaction, whereas "skarn" is used to describe a rock that is largely the result of metasomatic replacement of a carbonate protolith by a high fluid–rock interaction. Note that in marbles that have experienced high-grade metamorphism, the role of fluids can be controversial and this distinction may be unclear (Valley et al. 1990).

Zircons have been reported in marbles from several areas (Elsenheimer 1988; Ferry 1996; Tang et al. 2006; Liu et al. 2006); marble is thus known to contain zircon and has an appropriate range of $\delta^{18}O$(whole-rock) to be a suitable source for the high $\delta^{18}O$ zircons. The hypothesis that marble is a source for high $\delta^{18}O$ zircons can be further evaluated based on oxygen isotope exchange considerations. The equilibrium fractionation factor for calcite-zircon calculated from published values for zircon-quartz and quartz-calcite yields $1{,}000\ \ln\alpha_{(\text{calcite-zircon})} = 2.26 \times 10^6/T^2$ (T in K, Valley 2003). This fractionation factor yields $\Delta^{18}O$(calcite-zircon) = 2.0–3.8‰ from 800 to 500°C (Fig. 6). In the following sections, $\delta^{18}O$ values of calcite from rocks in Mogok and Sri Lanka are compared with the zircon data to evaluate further marble as a potential source for the high $\delta^{18}O$ zircons.

Origin of Mogok high $\delta^{18}O$ zircons

The source of large zircons in the Mogok placer deposits has not been determined; however, the area is well known for the occurrence of gemstone deposits (corundum, spinel, forsterite) in amphibolite facies marbles of Tertiary age, as well as placer deposits of these minerals (Garnier et al. 2008). Mogok marbles yield $\delta^{18}O$(calcite) = 19.9–27.8‰ (Garnier et al. 2008; Yui et al. 2008), values typical for marine carbonate (Fig. 4b). Gemstones from Mogok marbles are also characterized by high $\delta^{18}O$, including rubies ($\delta^{18}O$ = 20.1–25.7‰), spinel ($\delta^{18}O$ = 19.7–22.2‰), and forsterite ($\delta^{18}O$ = 19.2–22.0‰); corundum from placer deposits, desilicated pegmatites, and gemstones from unknown source rocks range to lower values ($\delta^{18}O$ = 10.3–21.4‰) (Giuliani et al. 2005; Garnier et al. 2008; Yui et al. 2008) (Fig. 4b). The $\delta^{18}O$ values of the zircons measured in this study overlap with the gemstones, particularly for the higher zircon values (Table 3). Not all of the Mogok detrital zircons are from high $\delta^{18}O$ rocks; there appear to be several source rocks represented in the zircon population based on the range in $\delta^{18}O$(Zrn) from 9.4 to 25.5‰ (a single source would be required to preserve >15‰ in $\delta^{18}O$(whole-rock) variability and is viewed as unlikely). A weak correlation exists between $\delta^{18}O$(Zrn) and color; dark red-to-orange zircons ($n = 8$) are restricted to a narrower range from 12.6 to 15.8‰, whereas light yellow-to-green zircons span the entire range (see color images in

Table 3 Laser fluorination oxygen isotope analyses of detrital zircons from Mogok, Myanmar

Sample #	Aliquot (mg)	Color	$\delta^{18}O$	2 SD
Session 1: May 5, 2008 (n = 10)				
MOGOK 2o	2.12	Clear/lt. yellow	24.33	0.04
MOGOK 2 g	1.96	Clear/lt. green	23.44	0.04
MOGOK 1A	2.06	Clear/lt. yellow	23.10	0.04
MOGOK 2i	1.89	lt. yellow/olive green	21.89	0.04
MOGOK 1 k	2.16	Dark green	19.21	0.04
MOGOK 1H	2.68	lt. orange/honey yellow	17.96	0.04
MOGOK 2a	1.96	lt. orange	15.65	0.04
MOGOK 2j	2.15	lt. yellow	12.08	0.04
MOGOK 2b	2.80	lt. orange	10.72	0.04
MOGOK 2 h	2.31	lt. olive green	9.37	0.04
UWG-2	1.66		5.53	–
UWG-2	1.59		5.56	–
UWG-2	1.49		5.52	–
UWG-2, average ($n = 3$)			5.54	0.04
Session 2: May 6, 2009 ($n = 18$)				
Mogok 2L	2.88	Clear/lt. olive green	25.48	0.04
Mogok 2 M	2.95	Clear/lt. yellow	25.37	0.04
Mogok 1G	2.32	Clear/lt. yellow	25.09	0.04
Mogok 1D	2.49	lt. yellow/olive green	24.78	0.04
Mogok 1E	2.92	Clear/lt. green	22.38	0.04
Mogok 2D	2.40	Clear/lt. yellow	22.15	0.04
Mogok 2E	2.48	Clear/lt. yellow	21.77	0.04
Mogok 1i	2.56	lt. yellow/olive green	20.83	0.04
Mogok 1 J	3.02	lt. yellow/olive green	18.90	0.04
Mogok 2 N	2.53	Clear/lt. yellow	16.97	0.04
Mogok 1C	2.81	Dark yellow/olive green	16.68	0.04
Mogok 4H	2.65	Orange-red	15.85	0.04
Mogok 4F	2.92	Orange	15.83	0.04
Mogok 4D	2.66	Dark orange-red	14.27	0.04
Mogok 3D	3.15	Dark orange-red	14.21	0.04
Mogok 4C	2.64	Dark red	13.96	0.04
Mogok 3B	2.57	Two-tone: dark red to clear	12.82	0.04
Mogok 4E	2.85	Dark red	12.58	0.04
UWG-2	2.06		5.80	–
UWG-2	2.23		5.76	–
UWG-2	1.67		5.76	–
UWG-2	1.51		5.78	–
UWG-2, average ($n = 4$)			5.78	0.04

SD standard deviation, *lt.* light

Online Resource 2). Roughly half (16 of 29) of the Mogok detrital zircons have $\delta^{18}O > 18‰$ and are in oxygen isotope equilibrium with measured calcite at 700°C (Fig. 4b). Marble is thus interpreted as the source for the Mogok detrital zircons with $\delta^{18}O > 18.0‰$, whereas zircons with lower but still high $\delta^{18}O$ (9.4–17‰) could have originated in marble, skarn, or other lower $\delta^{18}O$ rocks.

Origin of Sri Lanka high $\delta^{18}O$ zircons

Zircon CJJ4

The $\delta^{18}O$ value of 19.4‰ makes CJJ4 the highest $\delta^{18}O$ zircon identified from Sri Lanka. CJJ4 is also the only high $\delta^{18}O$ zircon in this study with a known source

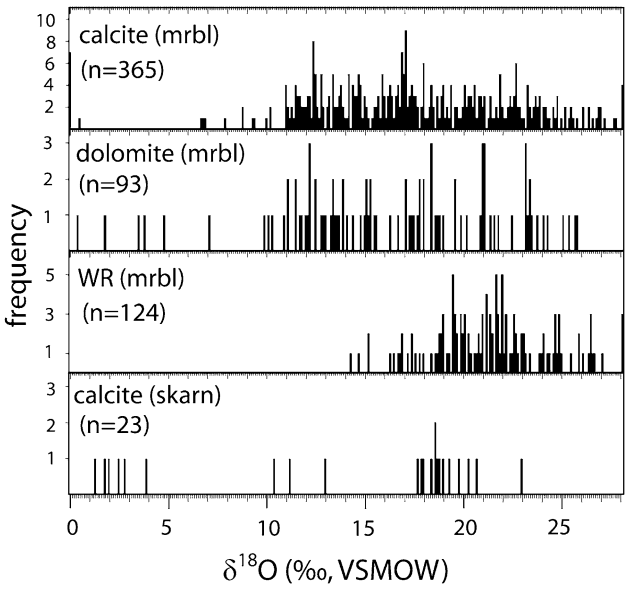

Fig. 5 Compilation of 605 oxygen isotope analyses of dolomite, calcite, and WR from amphibolite and granulite facies marbles and skarns. The data represent 20 different high-grade metamorphic terranes. *Mrbl* marble; *WR* whole rock. Data sources are listed in Online Resource 1

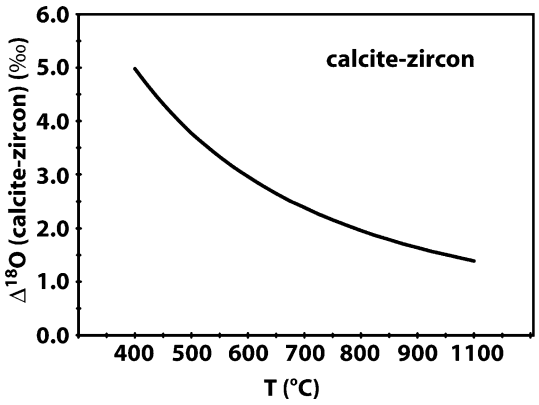

Fig. 6 Oxygen isotope equilibrium for calcite-zircon. The calcite-zircon fractionation factor is from Valley (2003)

rock—granulite facies marble. Previously reported δ^{18}O(calcite) values from granulite facies marbles from the Highland Southwest Complex (HSWC) of Sri Lanka yield δ^{18}O(calcite) = 15.9–24.4‰ (Elsenheimer 1988; Hoffbauer and Spiering 1994), values typical of high-grade marble (Fig. 5). The δ^{18}O(calcite) value of 23.6‰ measured by Elsenheimer (1988) for a bulk sample of calcite from the same hand sample as CJJ4 yields Δ^{18}O(calcite-zircon) = 4.2‰, corresponding to a temperature of 480°C if in equilibrium (Fig. 6). Zircon CJJ4 is euhedral and in textural equilibrium with calcite and tremolite (Fig. 2a); however, it is not in isotopic equilibrium with calcite at granulite facies temperatures. The non-equilibrium fractionation may indicate that the calcite is zoned at the centimeter scale, that is, the bulk calcite aliquot that yielded δ^{18}O = 23.6‰ may have contained calcite zoned with high and low δ^{18}O domains. Alternatively, the δ^{18}O value of this calcite may have been partially reset during granulite facies metamorphism or subsequent retrograde metamorphism. Taken together, the high δ^{18}O and absence of growth zoning are consistent with the petrographic occurrence of zircon CJJ4 as a metamorphic grain and provide "ground truth" that high δ^{18}O zircons can crystallize in marble.

Detrital zircon CZ3

Both CZ3 and M257 have U–Pb ages that coincide with the timing of Neoproterozoic granulite facies metamorphism at ca. 570–560 Ma in the HSWC (Kröner and Williams 1993; Hölzl et al. 1994). The compositions of CZ3 and M257 have previously been well characterized due to their use as standards in U–Pb geochronology, and thus additional geochemical data are available for evaluating marble as a source for these zircons based on the δ^{18}O values.

For CZ3, trace element abundances and ratios support a crustal origin, including high U (551 ppm) and low Th/U (0.05) (Pidgeon et al. 1994; Nelson 1997; Belousova et al. 1998; Valley et al. 1998; Konzett et al. 2000; Belousova et al. 2002; Nasdala et al. 2004). The low average ΣREE abundance of 26 ppm for CZ3 (Mattinson et al. 2006) is not typical of igneous zircon from the crust; such low abundances have only been previously reported for zircons from kimberlite (Belousova et al. 1998; Spetsius et al. 2002; Page et al. 2007b) and carbonatite (Hoskin and Schaltegger 2003). The CART classification scheme for zircon provenance based on trace element composition (Belousova et al. 2002) suggests an origin for CZ3 in kimberlite; however, the high U, low εHf (Griffin et al. 2000), low Th/U, and high δ^{18}O of CZ3 clearly preclude an origin in the mantle. Separately, each trace element data set for CZ3 shows characteristics typical for igneous zircon from both the crust (U, εHf, δ^{18}O) and the mantle (ΣREE) and also for metamorphic zircon (Th/U). However, the combined trace element data for CZ3 are unlike any known igneous zircon (Hoskin and Ireland 2000; Belousova et al. 2002; Hoskin and Schaltegger 2003) and taken together with the high δ^{18}O and lack of growth zoning in CZ3 are consistent with a metamorphic petrogenesis in marble or skarn derived from marble. With a δ^{18}O value of 15.4‰, CZ3 is in equilibrium with measured δ^{18}O values of Sri Lanka calcite at temperatures from 700 to 800°C (Fig. 4a).

Detrital zircon M257

Zircon standard M257 has a δ^{18}O value of 13.9‰ (Nasdala et al. 2008), slightly lower than CZ3. M257 has a

$^{206}Pb/^{238}U$ age of 561 Ma, U abundance of 840 ppm, a Th/U ratio of 0.27, and it is unzoned (Nasdala et al. 2008). It contains ~1 ppm Li and has a δ^7Li value of 2.1 ± 1.0 (Li et al. 2011). No other trace element data have thus far been reported for M257. With a δ^{18}O of 13.9‰, M257 is marginally in equilibrium with the lowest measured δ^{18}O values of Sri Lanka calcite at temperatures of 700–800°C (Fig. 4a). The similarity of M257 to CZ3 in age, lack of growth zoning, and lower, but still high, δ^{18}O, indicates that M257 also originated as a metamorphic zircon in marble or marble-derived skarn.

Petrogenesis of high δ^{18}O zircons

Zircon was identified as a trace mineral in 5 of 33 granulite facies marbles from Sri Lanka by Elsenheimer (1988). In this paper, it is further demonstrated by in situ analysis that Sri Lanka granulite facies marble (sample CJJ4) contains high δ^{18}O zircon, here, interpreted to have crystallized during high-grade metamorphism. We propose that metamorphosed marble is a suitable source rock for the high δ^{18}O detrital zircons from Sri Lanka and Mogok analyzed in this study, based on the oxygen isotope systematics between zircon and calcite, and also from the results of other studies that have demonstrated the occurrence of zircon in marble. Tang et al. (2006) reported zircons in "impure marble" from the Sulu orogen (China) and interpreted their origin as detrital igneous grains, based on euhedral forms and the presence of oscillatory zoning. If detrital zircons provide the Zr for metamorphic zircon growth in high-grade marbles, a process of dissolution and reprecipitation is indicated; this is consistent with the absence of inherited zoning in the high δ^{18}O zircons reported here. Dissolution and reprecipitation may explain other occurrences and/or disappearances of zircon in marble. In the Ballachulish contact aureole (Scotland), zircon occurs as a trace phase in siliceous quartz-free dolomites, persisting until the baddeleyite isograd is encountered (Ferry 1996):

$$\text{zircon} + 2\ \text{dolomite} = \text{baddeleyite} + \text{forsterite} + 2\ \text{calcite} + 2\ CO_2$$

$$ZrSiO_4 + 2\ CaMg(CO_3)_2 = ZrO_2 + Mg_2SiO_4 + 2\ CaCO_3 + 2\ CO_2$$

Phase equilibria constraints demonstrate that zircon in the Ballachulish aureole is stable with dolomite at 3 kbar and at temperatures up to ~710°C (Ferry 1996; Ferry et al. 2002). The upper stability of zircon will reach higher temperature and pressure values in quartz-saturated calcitic marbles in the absence of dolomite. A "zircon in" reaction was not identified for the Ballachulish marbles; it is thus unclear if these zircons are detrital or metamorphic, as their zoning characteristics were not described. Zircon was also reported as an abundant accessory phase in high δ^{18}O marble dikes cross-cutting granulite facies rocks in the eastern Himalaya that were interpreted to be remobilized from metasedimentary carbonates (Liu et al. 2006); zircon zoning characteristics were not reported, so both detrital and metamorphic origins are possible.

The reports of zircon in marble described above include grains that range from 10 s to < 200 μm in length; thus the processes active during their formation may be applicable to the petrogenesis of high δ^{18}O zircon CJJ4 (Fig. 2), which at ~150 μm can be considered a "typical" size zircon. The above examples do not, however, describe the occurrence of megacrystic zircon in marble; the formation and/or (re)crystallization mechanisms may be very different for the large high δ^{18}O zircons from Mogok and Sri Lanka, some of which are >8 mm (Online Resource 2). Zircon megacrysts have been reported from numerous rock types, including kimberlites (Kresten et al. 1975; Valley et al. 1998; Page et al. 2007b), carbonatites, syenites, and alkali basalts (Hinton and Upton 1991; Sutherland 1996), and to a lesser extent granitic pegmatites. In all cases, the zircons have been interpreted as igneous grains that originated in mantle-derived melts based on the presence of oscillatory growth zoning (Page et al. 2007b; Ashwal et al. 2007; Siebel et al. 2009) and mantle-equilibrated oxygen isotope ratios (Valley 2003; Valley et al. 1998; Upton et al. 1999; Page et al. 2007b; Siebel et al. 2009).

The large detrital zircons from Sri Lanka and Myanmar described here are clearly distinguishable from previous reports of igneous zircon megacrysts based on their high δ^{18}O values and absence of growth zoning and may represent the first report of megacrystic zircon from metamorphic rocks (even though we emphasize the fact that their host rocks have not been identified). It is therefore likely that different crystallization processes were active during the solid-state formation of the high δ^{18}O metamorphic megacrysts compared with the igneous megacrysts. Several studies have addressed processes governing the growth, recrystallization, and coarsening of zircon in quartzite and metapelitic rocks, including Ostwald ripening and the role of anatectic melt enhanced Zr transfer (Nemchin et al. 2001; Ayers et al. 2003; Peck et al. 2010). Without knowledge of certain characteristics of the host rocks for the high δ^{18}O megacrysts (e.g., bulk composition, Zr content, zircon crystal size distribution), it is not possible to evaluate the influence of Ostwald ripening or the presence of partial melts during the formation of the megacrysts. However, we note that in the above three studies the amount of coarsening reported, whether by Ostwald ripening (Ayers et al. 2003) or in conjunction with melt transfer (Nemchin et al. 2001; Peck et al. 2010) did

not produce zircons larger than 250 μm (most are <100 μm), even when the overgrowth constituted 70% by volume of the grain. Moreover, in all cases, the newly precipitated overgrowths preserve readily identifiable growth zoning in CL images. It appears that both Ostwald ripening and/or partial melting in quartzite and metapelitic rocks, where documented, produce metamorphic zircons with markedly different internal zoning characteristics and grain sizes when compared with the high $\delta^{18}O$ zircon megacrysts from Sri Lanka and Mogok. A detailed investigation of the growth mechanisms for the high $\delta^{18}O$ megacrysts is beyond the scope of this paper and would require identification of the source rocks.

Conclusions

The $\delta^{18}O$ of zircon from high $\delta^{18}O$ marble is a readily identifiable isotopic fingerprint of the source. The $\delta^{18}O$ of 19.4‰ for zircon CJJ4 from this study confirms a metamorphic petrogenesis of zircon in marble. High $\delta^{18}O$ can be combined with other geochemical data for determining the provenance of detrital metamorphic zircon derived from carbonate rocks. Detrital zircons with $\delta^{18}O$ of 15‰ or higher are most likely to have originated in high $\delta^{18}O$ marble or skarn derived from marble. Metachert and metapelite can also be high $\delta^{18}O$ source rocks; however, high $\delta^{18}O$ zircons reported from these lithologies occur as rims around inherited igneous cores and are thus readily distinguishable from the large and unzoned grains described here. Targeting high $\delta^{18}O$ metamorphic zircon in marble for U–Pb analysis may provide more accurate determination of the timing of high-grade marble formation.

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