

Multiple origins of zircons in jadeitite

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Received: 17 May 2009 / Accepted: 5 October 2009 / Published online: 24 October 2009
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Abstract Jadeitites form from hydrothermal fluids during high pressure metamorphism in subduction environments; however, the origin of zircons in jadeitite is uncertain. We report ion microprobe analyses of $\delta^{18}\text{O}$ and Ti in zircons, and bulk $\delta^{18}\text{O}$ data for the jadeitite whole-rock from four terranes: Osayama serpentinite mélangé, Japan; Syros mélangé, Greece; the Motagua Fault zone, Guatemala; and the Franciscan Complex, California. In the Osayama jadeitite, two texturally contrasting groups of zircons

are identified by cathodoluminescence and are distinct in $\delta^{18}\text{O}$: featureless or weakly zoned zircons with $\delta^{18}\text{O} = 3.8 \pm 0.6\%$ (2 SD, VSMOW), and zircons with oscillatory or patchy zoning with higher $\delta^{18}\text{O} = 5.0 \pm 0.4\%$. Zircons in phengite jadeitite from Guatemala and a jadeitite block from Syros have similar $\delta^{18}\text{O}$ values to the latter from Osayama: Guatemala zircons are $4.8 \pm 0.7\%$, and the Syros zircons are $5.2 \pm 0.5\%$ in jadeitite and $5.2 \pm 0.4\%$ in associated omphacite, glaucophanite and chlorite-actinolite rinds. The $\delta^{18}\text{O}$ values for most zircons above fall within the range measured by ion microprobe in igneous zircons from oxide gabbros and plagiogranites in modern ocean crust ($5.3 \pm 0.8\%$) and measured in bulk by laser fluorination of zircons in equilibrium with primitive magma compositions or the mantle ($5.3 \pm 0.6\%$). Titanium concentrations in these zircons vary between 1 and 19 ppm, within the range for igneous zircons worldwide. Values of $\delta^{18}\text{O}$ (whole-rock) $\cong \delta^{18}\text{O}$ (jadeite) and vary from 6.3 to 10.1‰ in jadeitites in all four areas.

These values of $\delta^{18}\text{O}$ and Ti are higher than predicted for hydrothermal zircons, and the $\delta^{18}\text{O}$ values of most zircons are not equilibrated with the coexisting jadeite at reasonable metamorphic temperatures. We conclude that while some zircons may be hydrothermal in origin, a majority of the zircons studied are best explained as relic igneous crystals inherited from precursor rocks; they were not precipitated directly from hot aqueous fluids as previously assumed. Therefore, U–Pb ages from these zircons may date magmatic crystallization and do not establish the timing of high pressure metamorphism or hydrothermal activity.

Communicated by J. Hoefs.

Electronic supplementary material The online version of this article (doi:10.1007/s00410-009-0453-y) contains supplementary material, which is available to authorized users.

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Keywords Zircon · Jadeite · Hydrothermal ·
Oxygen isotopes · SIMS · Greece · Japan · Guatemala ·
California

Introduction

Jadeitites are rocks rich in jadeite that precipitated from hydrothermal fluids (mostly $\leq 450^\circ\text{C}$) either in veins or as metasomatic replacement of metamorphosed precursors at blueschist or eclogite facies within subduction complexes (Harlow et al. 2007 and references therein). The generally agreed upon hydrothermal genesis of jadeitites has led many to assume that their constituent minerals, including zircon, have a similar origin, and this hypothesis is supported by observations that are reported for some zircons including metamorphic mineral inclusions and trace element compositions (Tsujimori et al. 2005; Bröcker and Keasling 2006). These results have further been interpreted to indicate that geochronology of the zircons dates high pressure (HP) metamorphism. However, we show that not all zircons in jadeitite have these characteristics. Zircons are highly resistant to alteration under hydrothermal or high grade metamorphic conditions (Valley 2003; Page et al. 2007a), and thus it is possible that zircons in jadeitite could be inherited from pre-metamorphic protoliths. Zircons are increasingly recognized as primary igneous minerals in ocean crust (Grimes et al. 2007, 2009a, b; Cavosie et al. 2009), suggesting that many jadeitite zircons could be inherited from igneous rocks that were subducted and metasomatically replaced, and that these zircons date the time of magmatic crystallization at the Mid-ocean ridge. These zircons help constrain the formation and subduction history of ocean crust, and fluid-rock interactions during hydrothermal seafloor alteration and/or during the time period of subduction.

In this study, we report values of $\delta^{18}\text{O}$ and Ti measured in situ by ion microprobe from 10 μm spots on single zircons and values of $\delta^{18}\text{O}$ measured in bulk from host jadeitites. Our investigation builds on previous studies of jadeitite zircons from the same samples, which proposed a hydrothermal/metasomatic origin. The new geochemical data are compared to compositions of igneous zircons from likely protoliths and to predicted compositions for hydrothermal zircons in order to test whether they crystallized during magmatic crystallization or later HP metamorphism. We conclude that many of the zircons studied were not precipitated from aqueous fluids as previously assumed and are best explained as relic igneous crystals inherited from pre-metamorphic igneous protoliths.

Sample descriptions

Jadeitite was studied from four well-documented areas: (1) Osayama, SW Japan (Tsujimori et al. 2005); (2) Syros, Greece (Bröcker and Keasling 2006); (3) the Motagua Fault zone, Guatemala (Harlow et al. 2004); (4) New Idria

in the Franciscan Complex, California (Coleman 1961; Tsujimori et al. 2007). Despite a thorough search, no zircons were found in our samples of the New Idria jadeitite veins or immediate blueschist host rock. Nevertheless, we report new whole-rock oxygen isotope results for early jadeitite and late albite veins and associated host rocks collected for this work; these are useful for comparative purposes. The investigated samples and geochronology of selected localities are described in detail in Electronic supplementary material (ESM) S1.1; we give a brief summary on zircons below.

Two types of zircon in jadeitite have been identified from Osayama, SW Japan, by Tsujimori et al. (2005) based on cathodoluminescence (CL) imaging and ion microprobe U–Pb dating. The ig-type zircons (i.e., Type II of Tsujimori et al. 2005) have zircon cores with concentric, oscillatory or patchy CL zoning (Fig. 4 of Tsujimori et al. 2005) and relatively high Th/U ratios from 0.73 to 0.83, and give an average U–Pb age of 507 ± 39 Ma ($n = 3$). The h-type zircons (i.e., Type I of Tsujimori et al. 2005) occur as entire zircon crystals or rimming ig-type zircons, and show featureless or weak CL zoning (see Fig. 4 of Tsujimori et al. 2005). H-type zircons have lower Th/U ratios mostly between 0.19 and 0.57, and yield an average U–Pb age of 479 ± 44 Ma (2 SD, $n = 25$). In a thin section of Osayama jadeitite, one zircon that is believed to be h-type based on its CL pattern contains inclusions of rutile and jadeite (see Fig. 2 of Tsujimori et al. 2005). Both ig-type and h-type zircons are interpreted to be hydrothermal by Tsujimori et al. (2005).

Zircons from a jadeitite block and associated metasomatic alteration rinds (omphacitite, glaucophanite and chlorite-actinolite schist) from Syros, Greece, have been studied by Bröcker and Keasling (2006). Most of the zircons display regular oscillatory or sector zoning, or homogenous featureless domains. The zircons from this suite of mélange samples as well as from a vein-fractured metabasic host rock (M. Bröcker, unpublished data) yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 79.6 to 79.8 Ma, and are proposed to have formed from hydrothermal fluids during HP metamorphism (Bröcker and Keasling 2006).

Zircons from the Guatemalan phengite jadeitite sample MVE02-8-6 are ~ 70 to 100 μm in size and display regular oscillatory or sector zoning, or homogenous featureless domains (see Fig. S1.1). There is no obvious core-rim texture as commonly seen in HP metamorphic rocks.

Analytical methods

Bulk oxygen isotope analyses of whole-rock, jadeite and albite separates were performed at the University of Wisconsin, Madison, by laser fluorination as described by

Table 1 Comparison of texture and chemistry for zircons from jadeitite from Osayama, SW Japan; Syros, Greece; and Guatemala

	Osayama, SW Japan	Osayama, SW Japan	Syros, Greece	Guatemala
Lithology	Jadeitite	Jadeitite	Jadeitite	Phengite jadeitite
Type of zircon	h-type	ig-type		
Size of crystals	~1 mm	~1 mm	~150–200 μm	<100 μm
Morphology	Euhedral	Sub-euhedral	Euhedral	Euhedral
CL texture	Featureless or weakly zoned	Oscillatory or concentric zones	Concentric or sector zones	Oscillatory zones
Mineral inclusions	Jadeite, rutile	Not observed	Not observed	Rare, not identified
Fluid inclusions	Not observed	Not observed	Not observed	Not observed
Th (ppm)	1.2 to 37, and 81 ($n = 35$)	45 to 68 ($n = 3$)	5 to 1,096 ($n = 15$)	18 to 5,900 ($n = 5$)
U (ppm)	6.4 to 94, and 149 ($n = 35$)	64 to 85 ($n = 3$)	16 to 737 ($n = 15$)	120 to 2,290 ($n = 5$)
Th/U (ratio)	0.19 to 0.57, and 1.20	0.73 to 0.83	0.32 to 1.54	0.04 to 2.57
U–Pb age (Ma)	531 to 370 ($n = 35$)	527 to 488 ($n = 3$)	77 to 83 ($n = 15$)	154 ($n = 8$)
$\delta^{18}\text{O}$ (‰) range	3.2 to 4.4	4.6 to 5.4	4.6 to 5.5	3.9 to 5.4
Average (± 2 SD)	3.8 ± 0.6 ($n = 95$)	5.1 ± 0.4 ($n = 28$)	5.2 ± 0.5 ($n = 28$)	4.8 ± 0.8 ($n = 21$)
$\Delta^{18}\text{O}_{\text{Jd-Zrc}}$ (‰)	4.0 or 5.7	2.8 or 4.4	1.8	2.5
$\epsilon_{\text{Hf}}(t)$	~+10	~+7	n.d.	n.d.
REE total (ppm)	75 to 340	460 to 640	n.d.	2,950 to 6,400
(Sm/La) _N	4 to 120	86 to 144	n.d.	205 to 4,461
Ce/Ce*	6 to 46	62 to 77	n.d.	15 to 409
Eu/Eu*	0.64 to 1.30	0.63 to 0.71	n.d.	0.07 to 0.45
Ti (ppm)	2.3 to 7.8 ($n = 12$)	1.0 to 3.2 ($n = 14$)	4.2 to 14 ($n = 22$)	4.5 to 19 ($n = 11$)
Origin of zircon	Hydrothermal/metasomatic	Inherited igneous	Inherited igneous	Both inherited and hydrothermal

Data sources: Tsujimori et al. (2005), Bröcker and Keasling (2006) and this study. *Jd* jadeite or jadeitite whole rock ($\delta^{18}\text{O}$ values, see Table 2), *Zrc* zircon ($\delta^{18}\text{O}$ values, see Electronic supplementary material S2)

n.d. no data

Valley et al. (1995) and Spicuzza et al. (1998). All $\delta^{18}\text{O}$ values are reported relative to Vienna Standard Mean Ocean Water (VSMOW). Six zircon grains were separated from the Guatemalan phengite jadeitite sample MVE02-8-6 (~2 cm³) that were treated in HF at room temperature for 21 days and handpicked from the residues. The zircons were imaged using a JSM-6360LV scanning electron microscope (SEM) with a Centaurus CL detector at Colgate University before in situ analysis. Ion microprobe analyses of $^{18}\text{O}/^{16}\text{O}$ ratios and trace element (Ti, REEs—rare earth elements, U and Th) concentrations in zircons were made on a CAMECA IMS-1280 ion microprobe at the University of Wisconsin, Madison. Analytical procedures were reported previously (Page et al. 2007b; Kita et al. 2009; Valley and Kita 2009). The locations of ion microprobe pits for oxygen isotopes and Ti concentrations were correlated, when applicable, with the SHRIMP U–Pb pits for the Osayama and Syros zircons. Laser ablation U–Pb and hafnium isotope analyses for the Guatemalan and Osayama zircons, respectively, were carried out (after ion microprobe analyses) at the University of Melbourne, using the 193-nm excimer laser-based HELEX ablation system equipped with two inductively coupled plasma mass spectrometers (ICP-MS) described in Woodhead et al.

(2004), Hellstrom et al. (2008) and Paton et al. (2009; see also ESM S1.2). The results were calibrated with the standard zircons 91500, Temora, BR-266 and KIM-5 (Wiedenbeck et al. 1995; Black et al. 2003a, b, 2004; Woodhead et al. 2004; Cavosie et al. 2005).

Results

The current and existing results for the jadeitite zircons are summarized in Table 1, and whole-rock and mineral oxygen isotope compositions for jadeitites and associated blackwall alteration zones are listed in detail in Table 2. All ion microprobe and ICP-MS results ($^{18}\text{O}/^{16}\text{O}$, Ti, REEs, $^{176}\text{Hf}/^{177}\text{Hf}$, U–Pb) for zircons from Osayama, Japan, Guatemala and Syros, Greece are listed in ESM S2 to S6. The average $\delta^{18}\text{O}$ values for individual zircons are summarized in Table 3.

Osayama, Japan

Whole-rock oxygen isotope ratios of jadeitites from Osayama are relatively high, 7.8 and 9.5‰ (Table 2), considerably above those in fresh igneous rocks from

Table 2 Whole-rock and mineral oxygen isotope ratios of jadeitites and associated rocks analyzed by laser fluorination

Sample	Lithology	$\delta^{18}\text{O}$ (‰) VSMOW	$\delta^{18}\text{O}$ (‰) Average
Osayama, SW Japan			
OSJ-A	Jadeitite WR	9.79, 9.15	9.47
OSJ-B	Jadeitite WR	7.83, 7.77	7.80
Syros, Greece			
3148 (A)	Jadeitite WR	7.69	7.69
3148 (B)	Jadeitite WR	6.30	6.30
3149	Omphacitite WR	5.65	5.65
3150	Glaucophanite WR	6.65	6.65
3152	Chlorite-actinolite schist WR	5.91	5.91
Guatemala			
(A) MVE02-8-6	Jadeitite WR	7.31, 7.31	7.31
	Jadeite (HF, 24 h)	7.32, [7.36], [7.44]	
	Jadeite (HF, 6 days)	[7.49]	
	Jadeite (HF, 21 days)	[7.15], [7.15]	
(B) MVE02-39-6	Jadeitite WR	8.23, 7.97	8.05
	Jadeite (HF, 24 h)	8.12	
	Jadeite (HF, 6 days)	7.89	
New Idria, CA			
NIJ-Ab	Vein Albite	12.24, 12.11	12.18
NIJ-Jd	Vein Jadeite	10.08	10.08
NIJ-Host	Blueschist WR	10.19, 10.16	10.18

Whole-rock (WR) samples were analyzed by airlock (Spicuzza et al. 1998), except data in brackets performed in normal analysis chamber

modern ocean crust, but consistent with rocks altered by low temperature interaction with seawater (Eiler 2001). Within a single jadeitite hand sample (OSJ-A), whole rock $\delta^{18}\text{O}$ values of 9.2 and 9.8‰ show local heterogeneity at the centimeter scale.

Ion microprobe $\delta^{18}\text{O}$ results for the two morphological types of zircon from the Osayama jadeitites define homogeneous but distinct populations (Fig. 1a): h-type zircon analyses average $3.8 \pm 0.6\text{‰}$ (2 SD, $n = 95$), while ig-type zircons average $5.1 \pm 0.4\text{‰}$ ($n = 28$). The within-type $\delta^{18}\text{O}$ variations are comparable to the analytical precision for the KIM-5 zircon standard analyzed in the same mount (0.6‰, 2 SD, $n = 69$). A few of the Osayama zircon grains show resolvable core versus rim gradients in $\delta^{18}\text{O}$ (e.g., 1.5–2.0‰ for grain no. 11, Fig. 2). The range and spatial distribution seen in these zoned grains ($\delta^{18}\text{O} \sim 5\text{‰}$ in the core vs. $\sim 3.5\text{‰}$ in the rim) mimics the difference between ig-type and h-type zircons found in discrete grains and is correlative with the textural and U–Pb data of Tsujimori et al. (2005).

Titanium concentrations in Osayama zircons vary between 1.0 to 7.8 ppm (average: 3.5 ± 4.1 ppm, 2 SD, $n = 32$; ESM S3 and S4). The average measured Ti concentrations in ig-type and h-type zircons are distinctly different: 2.1 ± 1.5 ppm (2 SD, $n = 12$) versus 4.9 ± 3.9 ppm ($n = 12$) (Fig. 3). Uncorrected Ti-in-zircon

temperatures range from 600 to 700°C (Fig. 3; Watson et al. 2006, but see Fu et al. 2008).

Hafnium isotope ratios ($^{176}\text{Hf}/^{177}\text{Hf}$) are also bimodal and range from 0.282613 ± 29 (2 SE) in the ig-type zircons to 0.282813 ± 35 in the h-type zircons (ESM S5). These ratios correspond to average $\varepsilon_{\text{Hf}}(t)$ values of $+7.2 \pm 3.0$ (2 SE, $n = 4$) in ig-type and $+10.1 \pm 3.6$ ($n = 8$) in h-type zircons (Fig. 4), and to Lu–Hf model ages (T_{DM} ; DM, depleted mantle) of 910 to 750 Ma and 760 to 610 Ma, respectively. A line regressed through most of the data points ($N = 7$; not including one younger outlier, ~ 420 Ma) for h-type zircons in Fig. 4 has a correlation coefficient of 0.83, which suggests a hafnium model age of 570 Ma, coincident with the age of gabbroic dikes from serpentinized peridotites in the same mélangé (~ 560 Ma; Hayasaka et al. 1995).

Syros, Greece

In contrast to Osayama, a single age population of zircons is found in the jadeitite and associated metasomatic reaction rinds from Syros (~ 80 Ma; Bröcker and Keasling 2006). Likewise, CL textures, $\delta^{18}\text{O}$ and Ti of Syros zircons also define a single population (Figs. 1, 3; Table 1). The range in average $\delta^{18}\text{O}$ for all the measured Syros zircon grains is 4.6 to 5.6‰ ($5.2 \pm 0.3\text{‰}$, $n = 46$). Individual

Table 3 Average $\delta^{18}\text{O}$ values (‰VSMOW) for individual zircon grains from jadeitite and associated rocks measured by ion microprobe

Mount_sample_grain	Average $\delta^{18}\text{O}$	± 2 SD	No. spot analyses
Jadeitite, Osayama, SW Japan			
Tsujimori_OSJ_#1 (h-type)	3.46	0.24	($n = 2$)
Tsujimori_OSJ_#3C (ig-type)	5.24	0.35	($n = 3$)
Tsujimori_OSJ_#3R (h-type)	3.91	0.49	($n = 1$)
Tsujimori_OSJ_#5 (h-type)	3.95	0.58	($n = 6$)
Tsujimori_OSJ_#6 (h-type)	3.84	0.39	($n = 6$)
Tsujimori_OSJ_#7 (h-type)	3.69	0.25	($n = 9$)
Tsujimori_OSJ_#8 (ig-type)	5.27	0.10	($n = 5$)
Tsujimori_OSJ_#9 (h-type)	4.07	0.30	($n = 18$)
Tsujimori_OSJ_#10 (h-type)	3.87	0.28	($n = 10$)
Tsujimori_OSJ_#11C (ig-type)	5.04	0.27	($n = 13$)
Tsujimori_OSJ_#11R (h-type)	3.54	0.41	($n = 19$)
Tsujimori_OSJ_#12 (h-type)	3.97	0.32	($n = 2$)
Tsujimori_OSJ_#13 (h-type)	3.44	0.29	($n = 7$)
Tsujimori_OSJ_#14 (h-type)	3.95	0.43	($n = 7$)
Tsujimori_OSJ_#15C (ig-type)	4.85	0.48	($n = 7$)
Tsujimori_OSJ_#15R (h-type)	3.56	0.73	($n = 4$)
Tsujimori_OSJ_#16 (h-type)	4.09	0.11	($n = 3$)
Jadeitite, Guatemala			
WF018_MVE02-8-6_Zrc1	4.90	0.67	($n = 10$)
WF018_MVE02-8-6_Zrc2	4.27	1.16	($n = 2$)
WF018_MVE02-8-6_Zrc3	4.74	0.82	($n = 5$)
WF018_MVE02-8-6_Zrc4	4.45	0.23	($n = 2$)
WF018_MVE02-8-6_Zrc5	5.12	0.25	($n = 2$)
WF018_MVE02-8-6_Zrc6	4.96	0.20	($n = 1$)
Jadeitite, Syros, Greece			
Broecker-1_3148_2	5.29	0.33	($n = 2$)
Broecker-1_3148_4	5.11	0.46	($n = 2$)
Broecker-1_3148_6	5.19	0.41	($n = 3$)
Broecker-1_3148_7	5.11	0.34	($n = 1$)
Broecker-1_3148_8	5.23	0.64	($n = 3$)
Broecker-1_3148_9	4.90	0.34	($n = 2$)
Broecker-1_3148_10	4.62	0.34	($n = 1$)
Broecker-1_3148_12	5.29	0.18	($n = 3$)
Broecker-1_3148_14	5.27	0.18	($n = 2$)
Broecker-1_3148_15A	5.02	0.02	($n = 2$)
Broecker-1_3148_15B	5.37	0.27	($n = 2$)
Broecker-1_3148_16	5.46	0.24	($n = 1$)
Broecker-1_3148_19	5.11	0.41	($n = 2$)
Broecker-1_3148_20	4.98	0.51	($n = 2$)
Omphacitite, Syros, Greece			
Broecker-3_3149_7	5.17	0.48	($n = 3$)
Broecker-3_3149_10	5.16	0.73	($n = 2$)
Broecker-3_3149_15	4.96	0.14	($n = 2$)

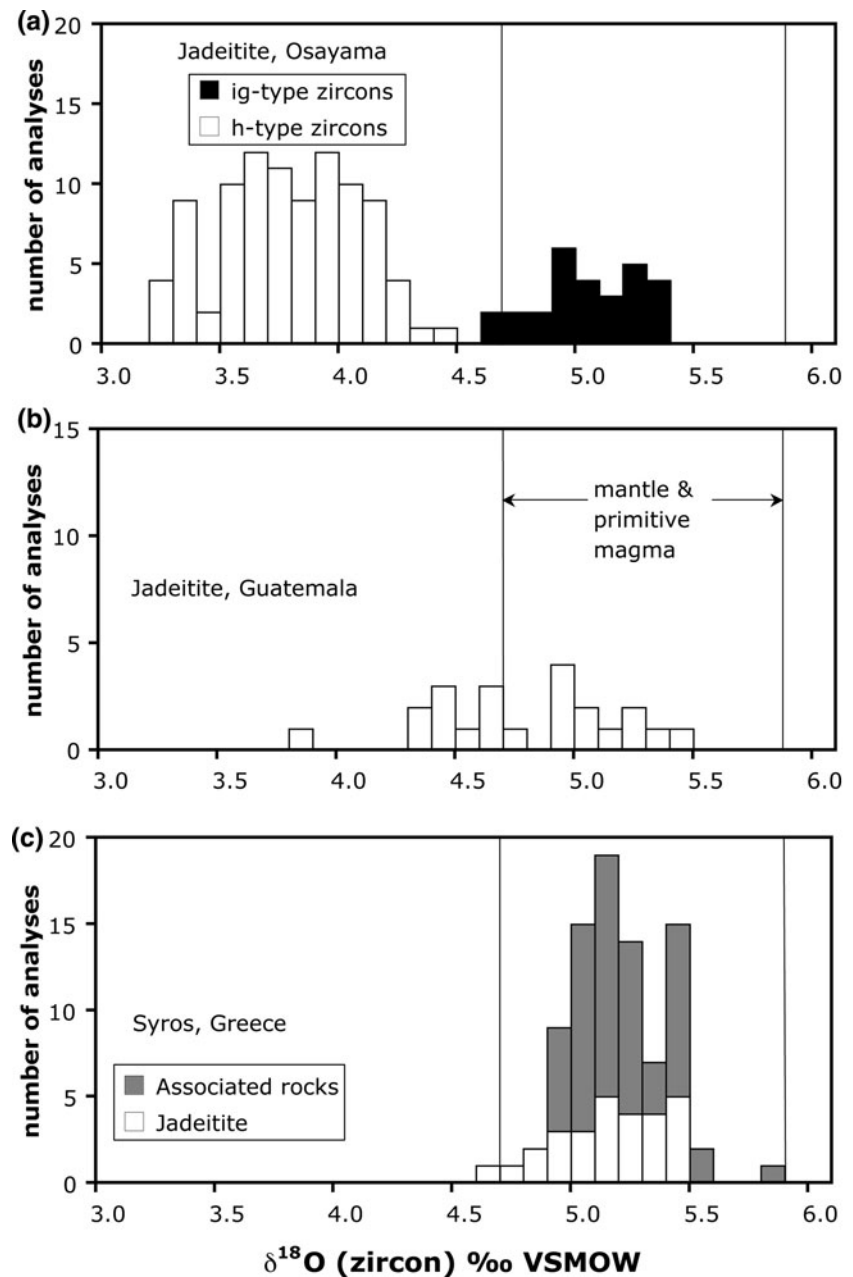
Table 3 continued

Mount_sample_grain	Average $\delta^{18}\text{O}$	± 2 SD	No. spot analyses
Broecker-3_3149_17	5.48	0.22	($n = 1$)
Broecker-3_3149_18	5.09	0.22	($n = 1$)
Broecker-3_3149_19	5.28	0.19	($n = 2$)
Broecker-3_3149_32B	5.62	0.60	($n = 2$)
Glaucofanite, Syros, Greece			
Broecker-3_3151_16A	5.23	0.56	($n = 2$)
Broecker-3_3151_17	5.11	0.06	($n = 2$)
Broecker-3_3151_20	5.24	0.74	($n = 2$)
Broecker-3_3151_6	5.31	0.25	($n = 3$)
Broecker-3_3151_7	5.48	0.10	($n = 2$)
Broecker-3_3151_9	5.23	0.25	($n = 1$)
Chlorite-actinolite schist, Syros, Greece			
Broecker-1_3152A_1	5.40	0.04	($n = 2$)
Broecker-1_3152A_3	5.10	0.20	($n = 1$)
Broecker-1_3152A_4	5.20	0.14	($n = 2$)
Broecker-1_3152A_6A	5.40	0.20	($n = 1$)
Broecker-1_3152A_7	5.14	0.20	($n = 1$)
Broecker-1_3152A_8	5.09	0.20	($n = 1$)
Broecker-1_3152A_11	5.03	0.20	($n = 1$)
Broecker-1_3152A_13	5.07	0.08	($n = 2$)
Broecker-1_3152A_15	5.18	0.34	($n = 3$)
Broecker-1_3152A_17	5.20	0.33	($n = 3$)
Broecker-1_3152A_18	5.29	0.20	($n = 1$)
Broecker-1_3152A_23	5.26	0.40	($n = 2$)
Broecker-3_3152B_3	5.20	0.06	($n = 2$)
Broecker-3_3152B_4A	5.11	0.30	($n = 2$)
Broecker-3_3152B_7	5.04	0.26	($n = 2$)
Broecker-3_3152B_9	5.16	0.07	($n = 2$)
Broecker-3_3152B_9B	5.10	0.27	($n = 1$)
Broecker-3_3152B_12	5.18	0.06	($n = 2$)
Broecker-3_3152B_16	5.02	0.15	($n = 2$)

Spot-to-spot reproducibility (2 SD) of KIM-5 standard during the sessions was typically better than 0.3‰

analyses for zircons from jadeitite average $5.2 \pm 0.5\%$ (2 SD, $n = 28$), identical to zircons from associated omphacitite, glaucophanite and chlorite-actinolite rinds ($5.2 \pm 0.4\%$, $n = 58$). Five spot analyses with anomalously low $\delta^{18}\text{O}$ (down to 3.3‰; ESM S2) are omitted from the averages given above. These anomalous values were measured in undated grains or domains showing a disturbed CL pattern similar to the much younger (~ 52 Ma) zircons reported in the same region by Tomaschek et al. (2003). It is possible that these five analysis pits represent domains of crystals that formed in a different manner from the main generation of zircons that were studied here. By comparison, whole-rock $\delta^{18}\text{O}$ for jadeitite and associated

Fig. 1 Histograms of $\delta^{18}\text{O}$ values analyzed by ion microprobe in zircons from jadeitite and associated rocks from **a** Osayama, SW Japan, **b** Guatemala and **c** Syros, Greece. All Syros and many Guatemalan zircons can be grouped with ig-type Osayama zircons and are interpreted in this study to be magmatic (see text). Note that igneous zircons from the mantle and in equilibrium with primitive magmatic compositions have values of $\delta^{18}\text{O} = 5.3 \pm 0.6\text{‰}$ (2 SD; Valley et al. 2005)



blackwall alteration zones in the Syros mélange vary from 5.7 to 7.9‰ (Table 2). At the centimeter scale, jadeitites from both Syros and Osayama vary by over 1.5‰ (Table 2), while the zircons are homogeneous within analytical uncertainty.

Our results are also consistent with laser fluorination results of Katzir et al. (2002) for bulk zircon separates from jadeitite on the island of Tinos, Greece ($\delta^{18}\text{O} = 5.01 \pm 0.01\text{‰}$) and from omphacitite on Syros ($\delta^{18}\text{O} = 5.09 \pm 0.06\text{‰}$, $n = 4$).

Titanium concentrations in the Syros zircons show considerable variability (3.3–16 ppm), and the ranges for zircons from different host rocks are comparable:

4.2–14 ppm (9.5 ± 5.4 ppm, 2 SD, $n = 22$) for zircon from jadeitite and 3.3–16 ppm (8.5 ± 6.8 ppm, $n = 42$) for zircon from associated rocks.

Guatemala

Values of $\delta^{18}\text{O}$ from jadeite mineral separates and jadeitite whole-rock were measured by laser fluorination. In order to concentrate jadeite, samples were leached with HF, and high purity jadeite separates were prepared by hand-picking. The $\delta^{18}\text{O}$ values of jadeite separates are indistinguishable from values for whole-rock samples that were not HF-treated (Table 2).

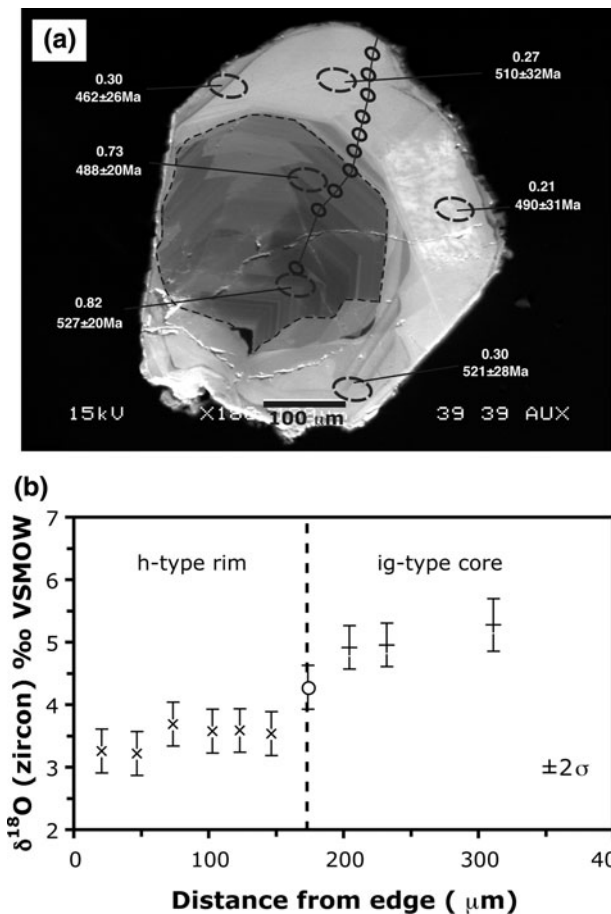


Fig. 2 CL image and oxygen isotope ratios measured in a traverse of a single zircon grain (no. 11, Tsujimori et al. 2005) from Osayama, SW Japan: **a** CL image, *small open symbols* show 10-μm-diameter ion microprobe oxygen isotope pits (many other O-pits are not shown here, see Electronic supplementary materials S2), *large dashed open symbols* show 25-μm U–Pb pits, *numbers* represent Th/U ratios and U–Pb ages (± 2 SE), *scale bar* 100 μm; **b** values of $\delta^{18}\text{O}$ from a core to rim traverse along the *solid line* in (a). Note that in this zircon, the core corresponds to ig-type zircon (Th/U > 0.3), and the rim is h-type zircon (Th/U ≤ 0.3) after Tsujimori et al. (2005), respectively. Ig-type zircon crystallized before h-type zircon, although U–Pb ages are indistinguishable within uncertainty of ± 38 Myr (2 SE)

Zircon oxygen isotope and trace element data were obtained for the Quebrada El Silencio phengite jadeitite. Values of $\delta^{18}\text{O}$ for individual zircons vary from 3.9 to 5.4‰. All spot analyses, if taken together, average $4.8 \pm 0.8\text{‰}$ (2 SD, $n = 22$), and the data are significantly more variable than zircons from Syros (Fig. 1b, ESM S2). Titanium concentrations in these zircons vary between 4.5 and 19 ppm (13 ± 10 ppm, 2 SD, $n = 11$). One measurement of 240 ppm Ti is unreasonably high for terrestrial zircons (mostly ≤ 20 ppm; Fu et al. 2008) and probably resulted from a Ti-rich inclusion (e.g., rutile).

Laser ablation ICP-MS U–Pb dating of the Quebrada El Silencio zircons yields a single grouping of data points just

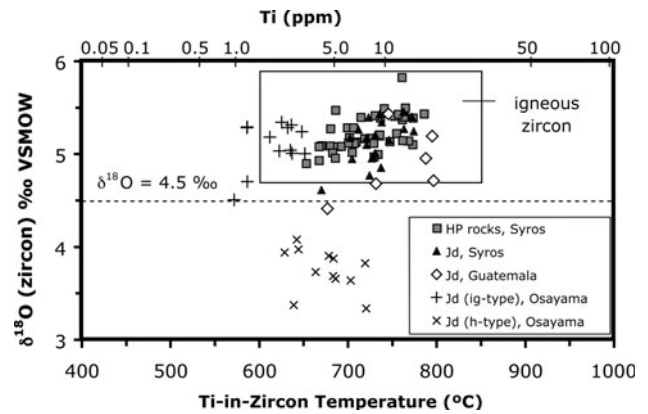


Fig. 3 Apparent Ti-in-zircon temperatures (uncorrected) and Ti concentrations versus $\delta^{18}\text{O}$ (zircon) from jadeitite and associated rocks from Syros, Greece; Guatemala; and Osayama, Japan. The *dashed line* ($\delta^{18}\text{O} = 4.5\text{‰}$) separates Osayama h-type zircons from ig-type zircons. Note that igneous zircons worldwide are shown by the *box*: values of $\delta^{18}\text{O}$ in equilibrium with mantle compositions are $5.3 \pm 0.6\text{‰}$ (2 SD; Valley et al. 2005) and apparent temperatures range from 600 to 850°C (Fu et al. 2008)

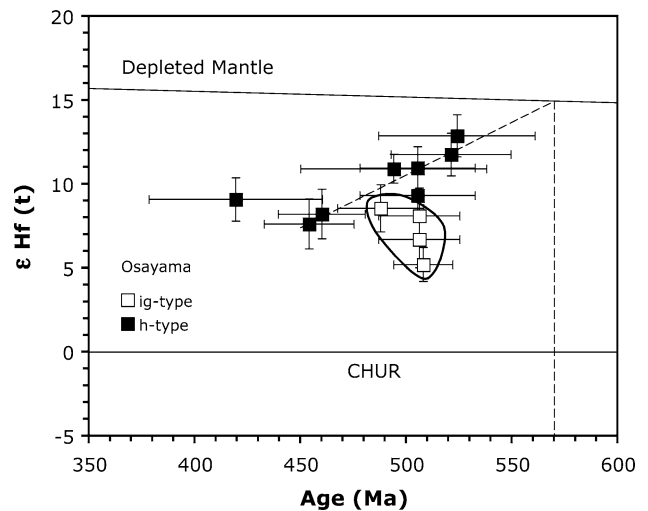


Fig. 4 Initial epsilon hafnium values of zircon ($\epsilon_{\text{Hf}}(t)$) versus in situ ion microprobe U–Pb ages from Osayama, SW Japan. The age data are taken from Tsujimori et al. (2005). *Error bars* are 2 standard errors. All data points lie between the CHUR (chondritic uniform reservoir) evolution line of the mantle and a MORB type reservoir, i.e., an increasingly LILE (large ion lithophile element)-depleted mantle. The regression line (*dash*, $R^2 = 0.83$) is defined by h-type zircons excluding one outlier and corresponds to the Hf isotopic evolution of source (or parent) igneous rocks extracted from the mantle at 570 Ma

above and overlapping concordia near 154 Ma (Fig. 5). After common Pb correction (using a 154-Ma model Pb composition; Stacey and Kramers 1975), the data points yield an average of 153.7 ± 3.5 Ma (2 SD, 8 out of 9 analyses; ESM S6). It appears that only one generation of zircon is present in this phengite jadeitite.

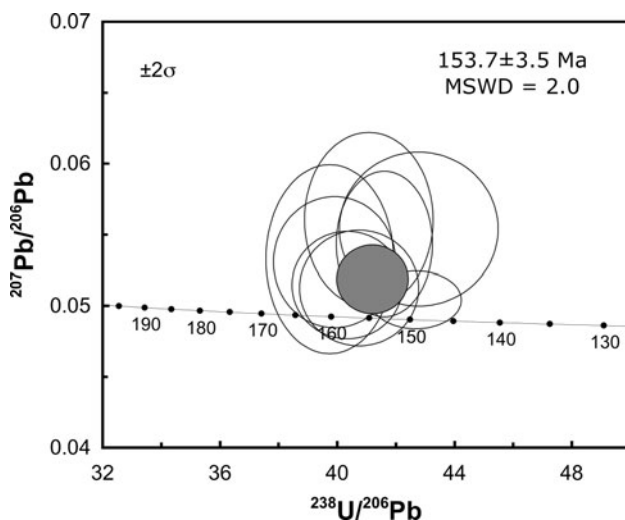


Fig. 5 Terra–Wasserberg concordia diagram of U–Pb for zircons from the Guatemalan phengite jadeitite. The initial common Pb isotopic composition of the zircons was estimated using the two-stage terrestrial Pb evolution model of Stacey and Kramers (1975) at 154 Ma. Data-points error ellipses are 2 SE

Franciscan Formation, New Idria, CA

A late albite vein from New Idria, CA, has a whole-rock $\delta^{18}\text{O} = 12.2\text{‰}$, whereas both an early jadeite vein and the adjacent blueschist have lower, but identical values of $\delta^{18}\text{O}$ (10.1–10.2‰) by laser fluorination.

Discussion

Zircons from igneous rocks

The $\delta^{18}\text{O}$ values of jadeitite zircons from this study can be compared to values found in igneous rocks that are likely protoliths to the jadeitite. The Syros zircons yield a uniform $\delta^{18}\text{O}$ value of $5.2 \pm 0.5\text{‰}$ (2 SD) from 86 analyses in four rocks. Likewise, the $\delta^{18}\text{O}$ values of ig-type zircons in the Osayama jadeitite are constant at $5.0 \pm 0.4\text{‰}$. The Guatemala zircons are more variable and may have formed by more than one process, but still the average is $4.8 \pm 0.8\text{‰}$ with many values above 4.7 (Table 3). These values are mostly identical within analytical uncertainty to those of igneous zircons measured by ion microprobe from oxide gabbros, norites and plagiogranites of modern ocean crust ($5.2 \pm 0.5\text{‰}$; Cavosie et al. 2009; Grimes et al. 2009b) and to igneous zircons measured in bulk by laser fluorination in high temperature equilibrium with primitive magma compositions or the mantle ($5.3 \pm 0.6\text{‰}$; Valley et al. 2005) (Fig. 1a–c).

In contrast to ig-type, the h-type zircons from Osayama average $3.8 \pm 0.6\text{‰}$, which is distinctly lower than normal

igneous zircons. Only a few of the grains from the Osayama jadeitite appear to incorporate both ig-type and h-type zircons. When both types are found in one crystal, the h-type zircon forms the rims and has lower $\delta^{18}\text{O}$ values than the ig-type zircon cores (e.g., zircon no. 11 in Fig. 2). This relation suggests that igneous zircon cores are overgrown by hydrothermal or metamorphic zircon rims.

Compared to the zircons, jadeitite whole-rock $\delta^{18}\text{O}$ values are much more variable. Overall, $\delta^{18}\text{O}$ values of jadeite grains or jadeitite whole rock from Osayama, Guatemala, Syros, and New Idria, CA, vary from 7.0 to 10.1‰. Here, we assume $\delta^{18}\text{O}$ (WR) \cong $\delta^{18}\text{O}$ (jadeite) because the jadeitites consist of over 90 modal percentage jadeite. These data are consistent with published jadeite $\delta^{18}\text{O}$ values of 8.0 to 9.4‰ from Guatemala (Johnson and Harlow 1999). However, these values are higher than whole-rock $\delta^{18}\text{O}$ values of 3.4 to 6.4‰ for meta-gabbros and HP rocks (e.g., omphacitite) from Syros (Putlitz et al. 2000; Katzir et al. 2002), which represent ocean crust that was hydrothermally altered by seawater on an ocean ridge at higher temperatures than the jadeitites of this study. Additional variability may result from fine-scale zoning. Sorensen et al. (2006) report large (>4‰) variations within individual CL-zoned jadeite crystals in jadeitites from Guatemala, California, SW Japan, Burma and Kazakhstan.

Oxygen isotopic disequilibrium

The fractionation of $\delta^{18}\text{O}$ between zircons and jadeite host rock provides a further test of the processes of formation. If both zircon and jadeite precipitated from the same hydrothermal fluid, they would be expected to be in isotopic equilibrium. These two minerals have slow oxygen diffusion rates and should preserve primary compositions (Valley 2001); in particular, zircons have been demonstrated to be refractory and highly retentive, retaining their magmatic O-isotope values through high-grade metamorphism and intense hydrothermal alteration (Valley 2003; Page et al. 2007a).

The equilibrium oxygen isotope fractionation between jadeite and zircon can be quantified from calibrations of quartz/jadeite and quartz/zircon equilibria (Matthews et al. 1983; Valley et al. 2003):

$$\begin{aligned} \delta^{18}\text{O}_{\text{Jd}} - \delta^{18}\text{O}_{\text{Zrc}} &= \Delta^{18}\text{O}_{\text{Jd-Zrc}} \approx 1000 \cdot \ln(\alpha_{\text{Jd-Zrc}}) \\ &= 1.55 \times 10^6 / T^2 (T \text{ in K}) \end{aligned} \quad (1)$$

Based on this relation, $\Delta^{18}\text{O}_{\text{Jd-Zrc}}$ is 3.0‰ at 450°C and 1.6‰ at 700°C.

The oxygen isotope fractionations measured in jadeitites of this study are highly variable (Table 1); $\Delta^{18}\text{O}_{\text{Jd-Zrc}}$ is: 1.8‰ for the Syros jadeitite, 2.5‰ for the Guatemalan phengite jadeitite, 2.8 or 4.4‰ (ig-type) and 4.0 or 5.7‰

(h-type) for the Osayama jadeitite. If equilibrated, these results would correspond to apparent oxygen isotope temperatures from 655 to 250°C (Eq. 1), indicating that many of the zircons are out of oxygen isotope equilibrium with the coexisting jadeites for metamorphic temperatures of $\leq 450^\circ\text{C}$ (Harlow et al. 2007). However, such estimates are further complicated by heterogeneity of $\delta^{18}\text{O}$ in jadeitite found in this study and by Sorensen et al. (2006). Oxygen isotope fractionations have been measured also for coexisting albite and jadeite. For the New Idria samples, one albite-jadeite pair ($\Delta^{18}\text{O}_{\text{Ab-Jd}} = 2.1\text{‰}$) would indicate an apparent temperature of 257°C, based on the calibration of Matthews et al. (1983). Furthermore, Sorensen et al. (2006) report $\Delta^{18}\text{O}_{\text{Ab-Jd}}$ values ranging from 7.7 to 2.6‰, with apparent temperatures of 6° to 209°C from two samples from Burma. Such low and variable apparent temperatures demonstrate oxygen isotopic disequilibrium conditions for albite and jadeite in these rocks. We note that jadeite in the Burmese samples studied by Sorensen et al. (2006) is in direct contact with albite, while this is not the case at New Idria.

Overall, the oxygen isotope ratios in jadeitite are characterized by variable and high $\delta^{18}\text{O}$ in jadeite crystals, centimeter-size chips of whole rocks and in decimeter-size whole rocks, and an apparent lack of oxygen isotope equilibrium among coexisting minerals. This variability contrasts with the values of $\delta^{18}\text{O}$ for zircons within jadeitites, which are uniformly lower and in most cases fall in the narrow range of 4.5 to 5.5‰. These results suggest that many zircons formed by a different process than jadeite.

Origin of zircons

Most $\delta^{18}\text{O}$ values in zircons in this study (excluding Osayama h-type zircons and possibly some Guatemala zircons) fall within the narrow range of zircon values from oxide gabbros, norites and plagiogranites of modern ocean crust (Cavosie et al. 2009; Grimes et al. 2009b). This fact suggests that these zircons are remnants from the igneous protoliths of jadeitite, or possibly detrital igneous zircons incorporated into the magmas, and that during metasomatic replacement the zircons remained unaffected. In contrast, the $\delta^{18}\text{O}$ values of host jadeitites are more variable and not in isotopic equilibrium, indicating that jadeite formed at a different, presumably later time.

Alternatively, if the uniform compositions of most jadeitite zircons resulted from hydrothermal/metasomatic processes, then it would be necessary that zircon crystallized at a narrow range of temperatures and from fluids, which resulted in a narrow range of values that fortuitously match igneous zircons, while the jadeites are highly variable in $\delta^{18}\text{O}$.

Other lines of evidence for the formation of zircons in jadeitite include chemical compositions, mineral inclusions and geochronology. Firstly, titanium concentrations for all the analyzed zircons, 1 to 19 ppm, are indistinguishable from known igneous zircons (mostly ≤ 20 ppm; Fu et al. 2008). If accurate, the Ti-in-zircon thermometer (Watson et al. 2006; Ferry and Watson 2007) indicates that zircons in phengite jadeitite from Guatemala, which contains quartz and rutile, crystallized at higher temperatures (average 760°C) than the formation of jadeitite (mostly $\leq 450^\circ\text{C}$; Harlow et al. 2007). While application of this thermometer is not fully constrained, especially in other samples that may not contain quartz or rutile, when Ti-in-zircon temperatures are not in agreement, they are generally lower than other independent estimates for crystallization of igneous rocks (Fu et al. 2008; see ESM S1.3).

Secondly, our preliminary trace element results indicate that some zircons from Guatemala and Osayama share similar characters with typical igneous zircons from either ocean crust or continental crust with regard to rare earth element patterns and trace element concentrations or ratios, possibly implying multiple origins of zircons in jadeitite. Moreover, trace element data further suggest that ig-type Osayama zircons (and some Guatemalan zircons), unlike h-type zircons, are most likely to be of magmatic origin (see ESM S1.4).

Thirdly, the mineral inclusion assemblages in the h-type Osayama zircons are diagnostic; jadeite and rutile clearly link h-type zircons to the jadeitite-forming event. However, no mineral inclusions have been identified within ig-type Osayama zircons or Guatemalan zircons. Furthermore, mineral inclusions could form by replacement of other inclusions after zircon growth. At Syros, the presence of glaucophane and omphacite inclusions in some zircons from glaucophanite led Bröcker and Keasling (2006) to conclude that all the zircons from the Syros jadeitite and associated metasomatic reaction rinds formed during the Cretaceous HP metamorphism. Most zircons were examined in two dimensions (e.g., thin sections), and it may be that re-examination of these zircons by high-resolution CL imaging and/or confocal laser Raman microscope will distinguish between cognate mineral inclusions and minerals that grew along cracks or in cavities within zircon grains during the jadeitite-forming event.

Finally, zircon ages provide direct criteria for genesis, if the timing of magmatism and metamorphism in the region is well constrained. Although the U–Pb age ranges of h-type and ig-type zircons from the Osayama jadeitite overlap: 531 ± 38 (2 SE) to 447 ± 18 Ma, and 527 ± 20 to 488 ± 20 Ma (Tsujimori et al. 2005), the age range for the h-type zircons is much larger, extends to younger ages and they give a lower average age (~ 480 Ma) than ig-type zircons (~ 510 Ma). Furthermore, ig-type zircons occur as

cores in some h-type zircons (the reverse relation has not been observed) and are therefore demonstrably older than h-type zircons. If the calculated hafnium model age of the Osayama h-type zircons is geologically meaningful despite their complex history (magmatism, metasomatism, metamorphism and/or hydrothermal alteration), hafnium was remobilized from igneous protoliths of jadeitite and thus the model age may represent the timing of melt (ultimate source) differentiated from the mantle at ~ 570 Ma (Fig. 4). In this regard, the fluids responsible for formation of h-type zircons may have interacted extensively with serpentinized peridotites or mafic rocks in the same mélange. Elsewhere, the presence of two types of zircon in jadeitite is supported by a recent study employing in situ ion microprobe U–Pb dating. Shi et al. (2008) identified two generations of zircon in jadeitite from Myanmar: 163.2 ± 6.6 Ma (2 SE) for inherited zircons and 146.5 ± 6.8 Ma for hydrothermal zircons, with one younger outlier (122.2 ± 9.6 Ma). It is noted that $\varepsilon_{\text{Hf}}(t)$ values for all these Burmese zircons are very high, from +15.5 to +20.0, interpreted to be derived from rapid reworking of very juvenile crust (Shi et al. 2009).

The zircon U–Pb age (154 Ma) for the Guatemalan phengite jadeitite is older than published $^{40}\text{Ar}/^{39}\text{Ar}$ ages of phengitic mica in diverse HP rock types from the south side of the Motagua Fault Zone, Guatemala (125 to 113 Ma; Harlow et al. 2004) or Sm–Nd mineral isochron ages of eclogites from both sides of the Motagua Fault Zone (125 to 141 Ma; Martens et al. 2007; Brueckner et al. 2009). This age difference (~ 10 to 40 Ma) indicates that the zircons in the Guatemalan phengite jadeitite grew prior to the Cretaceous HP metamorphism. Chiari et al. (2006) reported radiolarian biostratigraphic evidence for a Late Jurassic age of the (Río) El Tambor Group ophiolites in Guatemala. The HP rocks are interpreted as an exhumed subduction-channel boundary zone from a Cretaceous collision of the Chortís block with the North American plate and exposed adjacent to the Motagua Fault (Harlow et al. 2004; Brueckner et al. 2009), although there are other tectonic interpretations (e.g., Donnelly et al. 1990; Beccaluva et al. 1995; Solari et al. 2009).

Summary and conclusions

Based on morphology, textures, mineral inclusions, and/or chemical and isotopic compositions, zircons in jadeitite can be classified into two groups: the first group (hydrothermal/metasomatic) corresponds to h-type zircons from the Osayama jadeitite and the second group (remnant igneous zircon from protoliths) includes ig-type zircons from the Osayama, many zircons from the Guatemalan phengite jadeitite and all examined zircons from the Syros jadeitite

(and associated metasomatic reaction rinds). We conclude that the ig-type Osayama zircons, many Guatemalan zircons and the Syros zircons are inherited from pre-existing igneous rocks, and that only the h-type Osayama zircons and some of the low $\delta^{18}\text{O}$ Guatemalan zircons are consistent with a hydrothermal origin. Although previous petrogenetic studies have emphasized the importance of direct precipitation from hydrothermal fluids, the results of this study suggest that metasomatic replacement and alteration of pre-existing igneous rocks is important. Thus, zircons in eclogite facies rocks may have a more prolonged and more interesting history than previously thought.

Acknowledgments B. Hess helped with sample preparation, B. Selleck (Colgate University) assisted with SEM-CL imaging of the zircons from Guatemala, and A. Greig and J. Woodhead assisted with laser ablation ICP-MS analysis. R. Maas, I.N. Bindeman, four anonymous referees and the journal editor J. Hoefs reviewed an earlier version of this manuscript. This work was partly supported by the National Science Foundation (EAR-0509639, 0838058), US Department of Energy (93ER14389), and the Japan Society for the Promotion of Science, Grant-in-Aid for Young Scientists (B) (13740312) and for Scientific Research (B) (21340148). The Wisc-SIMS Laboratory is partially supported by the National Science Foundation (EAR-0319230, EAR-0516725, EAR-0744079).

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