

Eclogite-facies fluid infiltration: constraints from $\delta^{18}\text{O}$ zoning in garnet

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Abstract In situ analysis reveals that eclogite-facies garnets are zoned in $\delta^{18}\text{O}$ with lower values in the core and rims that are ~ 1.5 to 2.5 ‰ higher. This pattern is present in 9 out of 12 garnets analyzed by SIMS from four orogenic eclogite terranes, and correlates with an increase in the mole fraction of pyrope and Mg/Fe ratio from core to rim, indicating prograde garnet growth. At the maximum temperatures and the time-scales experienced by these garnets, calculated intragranular diffusion distances for oxygen are small (<5 μm), indicating that $\delta^{18}\text{O}$ records primary growth zoning and not diffusive exchange. The oxygen isotope gradients are larger than could form due to temperature changes during closed-system mineral growth. Thus, gradients reflect the compositions of fluids infiltrating during prograde metamorphism. Values of $\delta^{18}\text{O}$ in garnet cores range from -1 to 15 ‰, likely preserving the composition of the eclogite protoliths. Two garnet cores from the Almenningen eclogite in the Western Gneiss Region, Norway, have $\delta^{18}\text{O} \sim -1$ ‰ and are the first negative $\delta^{18}\text{O}$ eclogites identified in the region. In contrast with orogenic eclogites,

seven high $\delta^{18}\text{O}$ garnets (>5 ‰) from two kimberlites are homogeneous in $\delta^{18}\text{O}$, possibly due to diffusive exchange, which is possible for prolonged periods at higher mantle temperatures. Homogeneity of $\delta^{18}\text{O}$ in garnets outside the normal mantle range (5 – 6 ‰) may be common in kimberlitic samples.

Keywords Garnet · Eclogite · Oxygen isotopes · Zoning · Fluids · SIMS

Introduction

Numerous studies have proven the utility of oxygen isotope ratios for constraining the composition, timing, and flux of metamorphic fluids (e.g., Baumgartner and Valley 2001). Garnet is a common metamorphic mineral, stable to ultra-high temperatures and pressures. For many elements, growth zoning in garnet can be preserved at moderate to high temperatures recording the metamorphic P–T path. However, until recently, the technical difficulty in measuring oxygen isotopes in situ at μm -scales comparable to that attained by the electron microprobe has precluded combined studies of cation and $\delta^{18}\text{O}$ zonation.

Intragranular zoning of $\delta^{18}\text{O}$ in garnets at mm-scale coupled with major element compositions has suggested that finer-scale studies will provide a valuable tool for determining metamorphic fluid interactions (e.g., Kohn and Valley 1994). Infiltrating fluids from regions of contrasting composition or temperature will cause zoning of $\delta^{18}\text{O}$ during garnet growth. Oxygen-bearing fluid compositions can vary widely within a given tectonic setting, including mixtures of silicate melt, down-going surface waters, and devolatilization products. Recently, new instrumentation and analysis protocols allow accurate in situ analysis of

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$\delta^{18}\text{O}$ at 10 μm -scale in garnets by secondary ion mass spectrometry (SIMS) (Page et al. 2010).

Here, we report the first SIMS results for $\delta^{18}\text{O}$ in garnets from orogenic and kimberlite-borne eclogites. The purpose of this study is as follows: (a) to determine the magnitude and patterns of $\delta^{18}\text{O}$ zoning in garnet from eclogites and compare them to zoning of major elements, (b) to compare the $\delta^{18}\text{O}$ zoning in eclogite garnets from different orogens and a variety of geological settings, including orogenic eclogites and xenoliths in kimberlite, and (c) to examine the possible applications of zoning patterns to determining eclogite protoliths and fluid histories.

Genesis of eclogites

Eclogites are biminerale rocks consisting largely of omphacite and garnet and are found in orogenic belts, called orogenic eclogites, as well as xenoliths or xenocrysts in kimberlites. Orogenic eclogites occur in several settings, including lenses or boudins within crustal rocks, within peridotite massifs, and as members of mafic–ultramafic complexes, such as meta-ophiolites. Eclogites that reside within crustal rocks, including gneisses, granulites, and metasediments, are called external eclogites, in contrast to eclogites that occur as decameter- to centimeter-sized lenses and layers in peridotites, which are called internal eclogites (Medaris et al. 1995).

Eclogites are commonly interpreted to form by high-pressure (HP) metamorphism of mafic rocks in subducted oceanic or continental crust or during HP crystallization in primary mantle magmas. A range of $\delta^{18}\text{O}$ values is expected for oceanic crust protoliths, reflecting variable hydrothermal alteration. Ocean crust is dominated by mafic igneous rocks that initially have magmatic $\delta^{18}\text{O}(\text{WR})$ values of $5.5 \pm 0.6 \text{ ‰}$ (Eiler 2001). Such igneous rocks are commonly altered by hydrothermal interaction with seawater at variable temperatures on the oceanic ridge. Upper oceanic crust becomes higher in $\delta^{18}\text{O}$ (~ 6 to 12 ‰) due to low temperature ($<300 \text{ °C}$) exchange, and lower oceanic crust can become lower in $\delta^{18}\text{O}$ (~ 2 to 5 ‰) due to high temperature ($>300 \text{ °C}$) exchange (Gregory and Taylor 1981; Muehlenbachs 1986; Eiler 2001). Values less than 2 ‰ are possible, yet very rare. Upper oceanic crust also contains a thin veneer of very high $\delta^{18}\text{O}$ sediments. Values of $\delta^{18}\text{O}(\text{WR})$ below 1 ‰ have not been reported for altered oceanic crust, presumably due to low fluid/rock ratios at high temperature and fluids derived from seawater ($\delta^{18}\text{O} \sim 0 \text{ ‰}$). In continental crust, magmatic values of $\delta^{18}\text{O}$ in basalt are more variable (Harmon and Hoefs 1995), and exchange with heated meteoric water such that $\delta^{18}\text{O}(\text{WR})$ can produce values from -10 to $\sim 5 \text{ ‰}$ (Taylor and Forester 1979, Criss and Taylor 1986, Zhang et al.

1998). In contrast to the highly variable values of $\delta^{18}\text{O}$ that are expected for protoliths of subducted oceanic or continental crust, eclogites that form from high-pressure melts in the mantle are likely to have $\delta^{18}\text{O}(\text{WR})$ values that approximate that of mantle peridotites and pristine MORB ($5.5 \pm 0.6 \text{ ‰}$, Eiler 2001, Valley 2003; Cavosie et al. 2009; Grimes et al. 2011).

Some mantle eclogite xenoliths are interpreted to have crustal protoliths, as evidenced by a wide range in $\delta^{18}\text{O}$ values in garnet (2.5 – 9 ‰ , see Jacob 2004), which lie outside the normal mantle range for $\delta^{18}\text{O}(\text{WR})$ of $5.5 \pm 0.6 \text{ ‰}$. In addition, some coesite inclusions in E-type (eclogitic) diamonds yield $\delta^{18}\text{O}$ values $>10 \text{ ‰}$ (Schulze et al. 2003a). Data from some eclogite xenoliths display negative Eu anomalies, indicating the presence of plagioclase in the protolith (Jacob 2004). Further evidence for crustal origin in some eclogite xenoliths is provided by the wide range in $\delta^{34}\text{S}$ (Eldridge et al. 1991) and mass-independent sulfur isotope fractionations in sulfide inclusions in diamonds, a signature found in Archean crust and sediments (Farquhar et al. 2002). Satisfactory models do not exist to form such values in the mantle, as oxygen isotope fractionations are small at high temperatures, and pressure has no measureable effect on the fractionation of oxygen isotopes (Clayton et al. 1975). Although the majority of workers accept subducted oceanic crust as the precursor to at least some eclogite xenoliths, this interpretation is still debated (e.g., Griffin and O'Reilly 2007).

During subduction of mafic rocks along a prograde P–T path, garnet cores can inherit the $\delta^{18}\text{O}$ value of their protoliths (Putlitz et al. 2000), and garnet growth zoning records evidence of changing fluid and metamorphic conditions. For garnets in mafic rocks, the main control is fluid infiltration. The fractionation of oxygen isotopes between garnet and other minerals is small at high temperatures (see Chacko et al. 2001). Thus, closed-system garnet growth in metabasalt from 500 to 600 °C is predicted to increase in $\delta^{18}\text{O}$ by less than 0.2 ‰ from core to rim (Kohn et al. 1993). Likewise, fractionation due to devolatilization of basalt is small, being significantly less than 1 ‰ with rims slightly lower in $\delta^{18}\text{O}$ than cores (Valley 1986). In contrast to the relatively small thermal effects on $\delta^{18}\text{O}$ in mafic rocks, infiltration of fluids over large chemical and thermal gradients can cause significant zoning, especially for protoliths that are not mantle-like in $\delta^{18}\text{O}$ or if fluids are derived from high $\delta^{18}\text{O}$ sediments.

Geologic setting

To investigate a broad variety of eclogites, samples were selected from four orogenic belts and two kimberlites

(Online Resource 1). The orogenic eclogites (Table 1) vary in age, peak P–T conditions, and tectonic history: the Chatanika eclogite, Alaska; Saxothuringian and Moldanubian Zones, Bohemian Massif in central Europe; Western Gneiss Region, Caledonides, Norway; and Trescolmen, Adula Nappe, Eastern Alps, Switzerland (see Russell 2012).

For comparison with garnets from orogenic eclogites, garnets from eclogite xenoliths in kimberlite were selected for analysis. These samples are from eclogite xenoliths in the Roberts Victor kimberlite (Kaapvaal Craton, South Africa) and eclogitic garnet xenocrysts from the La Ceniza kimberlite (Guaniamo Region, Venezuela). Among Roberts Victor xenoliths, this study focuses on Group 1 coesite eclogites (Schulze et al. 2000; Jacob et al. 2003). Previous studies report values of $\delta^{18}\text{O}(\text{Grt})$ (2–8 ‰), positive Eu anomalies in garnet, and heterogeneous Hf, Sm–Nd, and Rb–Sr isotopic compositions, suggesting a subducted oceanic crust protolith. In contrast to Roberts Victor, the La Ceniza kimberlite contains only xenocrysts (Nixon et al. 1992; Kaminsky et al. 2004). A wide range in $\delta^{18}\text{O}$ (5.3–9.3 ‰) in garnet xenocrysts from disaggregated eclogites (Schulze et al. 2003b), high $\delta^{18}\text{O}$ values (10.2–16.9 ‰) for coesite inclusions in diamond (Schulze et al. 2003a), and low $\delta^{13}\text{C}$ values of diamond (Kaminsky et al. 2000) provides evidence of an oceanic crustal source for eclogite. Garnet grains with $\delta^{18}\text{O}$ values of either <4 ‰ or >6 ‰ were selected for detailed investigation.

Analytical methods

Laser fluorination

In order to identify garnets with $\delta^{18}\text{O}$ values different from those typical of the mantle, bulk garnet analyses were first undertaken. Samples (~10 g) were crushed and sieved. Clean garnet was handpicked under a binocular microscope. Aliquots of garnet (1.5–2.5 mg), and garnet standard, UWG-2, were pretreated with BrF_5 overnight prior to analysis. Using an IR laser ($\lambda = 10.6 \mu\text{m}$) and a Finnigan/MAT 251 gas-source mass spectrometer, garnets were fluorinated and CO_2 produced for analysis. Data are corrected to the VSMOW scale based on multiple analyses of UWG-2 garnet standard ($\delta^{18}\text{O} = 5.80 \text{ ‰ VSMOW}$, Valley et al. 1995). Laser fluorination results are found in Table 2 (for garnets) and Table 3 (for clinopyroxenes).

Imaging

Backscatter electron imaging with maximum contrast was used to locate the cores of concentric zoned garnets and to select garnets for SIMS analysis. In orogenic eclogite samples with compositionally zoned garnets, one or two representative garnets were chosen for SIMS and EPMA analysis. The garnets selected are devoid of major fractures, sieve texture, or abundant inclusions and display concentric zoning, favorable for SIMS analysis of both core and rim.

Table 1 Location and information for orogenic eclogite samples analyzed by SIMS

Sample	Locality	Terrane	Age (Ma)	Peak T (°C)	Peak P (kbar)	Structure
<i>Orogenic eclogites</i>						
89GM24A	Meluzína	Saxothuringia, Bohemian Massif, Czech Rep.	333–360 ^f	600–650 ^f	23.1–28.6 ^f	Boudin
MZ-1	Meluzína	Saxothuringia, Bohemian Massif, Czech Rep.	333–360 ^f	600–650 ^f	23.1–28.6 ^f	Boudin
TR00-27	Trescolmen	Adula Nappe, Alps, Switzerland	32.4 ± 1.3 ^e	550–650 ^e	15–25 ^e	Boudin
N87-15	Almenningen	Western Gneiss Region, Norway	420–440 ^c	611–629 ^d	27–28 ^d	Boudin
ST-2A	Šachotín	Moldanubia, Bohemian Massif, Czech Rep.	340 ^h	635–660 ^a	14–14.5 ^a	Boudin
PC-2	Poličany	Moldanubia, Bohemian Massif, Czech Rep.	340 ^h	615–730 ^a	13–14 ^a	Boudin
SP-1	Šlapanov	Moldanubia, Bohemian Massif, Czech Rep.	340 ^h	615–730 ^a	13–14 ^a	Boudin
SC-4	Spačice	Moldanubia, Bohemian Massif, Czech Rep.	340 ± 5 ^b	835–935 ^b	18–20 ^b	Boudin
FB23	Chatanika	Yukon-Tanana, Alaska	236 ± 1 ^g	523 ^g	14–15 ^g	Layered lens
FB26	Chatanika	Yukon-Tanana, Alaska	236 ± 1 ^g	523 ^g	14–15 ^g	Layered lens

^a Medaris et al. 1995

^b Medaris et al. 2006a

^c Krogh and Carswell 1995

^d Cuthbert et al. 2000

^e Liati et al. 2009

^f Klápková et al. 1998

^g Douglas et al. 2002

^h Sample undated, likely to be Variscan based on regional geology

Table 2 Garnet compositions by EPMA from cores and rims of garnets selected for SIMS and bulk $\delta^{18}\text{O}$ values

Sample	98GM24A		MZZ-1		TR00-27		N87-15 (C)		N87-15 (A)		FB23(1)		13-64-136		LCIG8		LC2G9	
	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim
SiO_2	37.68	38.99	38.45	38.90	37.38	40.13	38.94	41.71	37.95	41.08	37.59	37.91	40.38	39.81	42.48	42.55	41.73	41.83
TiO_2	0.18	0.09	0.04	0.07	0.21	0.02	0.07	0.01	0.10	0.02	0.34	0.05	0.23	0.27	0.19	0.16	0.36	0.32
Al_2O_3	20.62	22.44	21.71	22.33	21.07	22.84	21.79	23.29	21.26	23.30	21.37	21.70	22.73	22.01	23.88	23.74	23.21	23.11
FeO	24.87	21.97	23.54	21.89	27.19	21.36	25.38	15.17	24.34	15.60	27.66	26.41	18.43	18.34	8.71	8.49	10.17	10.12
MnO	1.37	0.42	1.36	0.27	1.50	0.17	1.28	0.12	1.91	0.07	0.91	0.75	0.43	0.45	0.38	0.27	0.38	0.29
MgO	1.66	7.37	3.98	7.61	2.60	7.12	4.41	14.40	4.11	13.35	2.21	2.16	13.49	14.62	20.64	20.21	19.79	19.66
CaO	12.91	8.90	10.79	8.06	8.70	8.26	9.22	6.40	9.19	7.10	10.78	11.19	4.48	4.24	4.39	4.47	3.75	3.81
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.14	0.14	0.50	0.38	0.62	0.61
Total	99.28	100.18	99.87	99.13	98.64	99.90	101.09	101.10	98.87	100.54	100.86	100.19	100.31	99.88	101.18	100.27	100.01	99.75
$X_{\text{Almandine}}$	54.4	46.8	50.4	48.2	61.1	46.4	54.8	25.9	52.8	32.1	59.7	58.2	37.9	36.5	16.9	16.8	20.1	20.1
X_{Pyrope}	6.5	28.0	7.5	27.9	10.4	29.5	17.0	61.8	17.0	49.0	8.5	8.5	49.4	51.8	71.4	71.3	69.7	69.6
$X_{\text{Grossular}}$	36.1	24.3	37.2	23.3	25.0	23.7	25.5	12.1	25.9	18.7	29.8	31.6	11.8	10.8	10.9	11.3	9.5	9.7
$X_{\text{Spessartine}}$	3.0	0.9	3.0	0.6	3.4	0.4	2.8	0.2	4.2	0.1	2.0	1.7	0.9	0.9	0.8	0.5	0.8	0.6
$\delta^{18}\text{O}^*$	2.44 ± 0.21		2.97 ± 0.11		8.18^a		-0.41 ± 0.13		-0.41 ± 0.13		13.73		6.34^b		No bulk value		No bulk value	No bulk value

Sample	ST-2A		PC-2		SP-1		SC-4		FB26		FB23(2)		13-64-122 (3)c		LC2G14		LC2G16	
	Mold. Zone	Rim	Mold. Zone	Rim	Mold. Zone	Rim	Mold. Zone	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim
SiO_2	37.72	37.73	36.60	38.29	39.53	39.92	38.89	39.71	37.25	38.39	37.25	37.86	40.33	40.63	42.90	42.84	40.07	39.77
TiO_2	0.09	0.02	0.10	0.02	0.08	0.06	0.09	0.07	0.16	0.11	0.16	0.04	0.27	0.30	0.45	0.44	0.35	0.33
Al_2O_3	21.55	21.95	21.18	21.74	21.77	22.15	21.97	22.24	21.24	21.97	21.12	21.69	22.71	22.79	24.03	23.93	22.45	22.31
FeO	21.19	25.34	27.10	25.00	18.13	18.11	21.53	20.45	28.83	25.13	29.13	26.51	18.57	18.89	7.76	7.49	20.15	20.16
MnO	3.28	0.52	0.44	0.94	0.60	0.44	1.18	0.40	0.91	0.38	0.65	0.80	0.50	0.57	0.22	0.38	0.45	0.42
MgO	4.56	5.91	2.97	5.32	5.21	5.29	5.90	7.20	1.93	3.51	1.94	2.21	10.29	10.16	21.94	21.55	11.75	11.82
CaO	10.24	7.38	9.72	7.50	14.83	15.03	10.02	9.79	8.81	10.94	9.66	11.47	7.94	7.77	3.78	3.83	5.19	5.23
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.07	0.05	0.01	0.06	0.00	0.16	0.12	0.08	0.08
Total	98.62	98.85	98.11	98.80	100.15	100.99	99.57	99.85	99.16	100.49	99.96	100.59	100.68	101.12	101.22	100.58	100.49	100.12
$X_{\text{Almandine}}$	46.3	55.2	59.8	55.5	38.5	38.3	46.7	44.2	64.8	54.9	63.9	57.7	39.0	39.7	14.9	14.6	41.8	41.7
X_{Pyrope}	17.8	23.0	11.7	21.1	19.8	19.9	22.8	27.8	7.7	13.7	7.6	8.6	38.5	38.1	75.3	75.0	43.5	43.6
$X_{\text{Grossular}}$	28.7	20.6	27.5	21.3	40.4	40.8	27.9	27.1	25.4	30.6	27.1	40.0	21.4	20.9	9.3	9.6	13.8	13.9
$X_{\text{Spessartine}}$	7.3	1.2	1.0	2.1	1.3	0.9	2.6	0.9	2.1	0.8	1.4	1.8	1.0	1.2	0.4	0.7	0.9	0.9
$\delta^{18}\text{O}^*$	1.82		1.36		3.75 ± 0.01		3.06		12.44 ± 0.13		13.73		6.95^b		No bulk value		No bulk value	No bulk value

Fe^{3+} calculated on the basis of 8 cations and 24 oxygen

* Bulk garnet laser values (‰, VSMOW) $\pm 2\text{SD}$

^a Wiesli (2002); ^b Schulze et al. (2000)

^c 13-64-122 (2) was found to have a similar composition to 13-64-122 (3), and no further analysis was done

Table 3 Clinopyroxene core and rim mineral compositions by EPMA and SIMS and bulk $\delta^{18}\text{O}$ values

Sample	98GM24A		MZ-1		TR00-27		N87-15C		SP-1		SC-4	
	Saxo. Zone	2	1	2	Trescolmen	1	2	Norway	Mold. Zone	1	2	Mold. Zone
Point	1	2	1	2	1	2	1	2	1	2	1	2
SiO ₂	56.00	55.76	54.21	55.03	56.53	56.51	55.68	55.77	54.54	53.81	52.16	51.48
TiO ₂	0.04	bd	0.07	0.05	0.06	0.07	bd	0.05	0.06	0.07	0.41	0.41
Al ₂ O ₃	9.57	9.61	7.34	9.61	12.13	12.51	8.23	8.01	1.73	1.91	11.30	9.85
FeO	3.74	3.85	6.60	5.70	2.84	3.01	2.11	2.20	3.55	4.09	6.77	7.41
MnO	0.04	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.05	0.08
MgO	9.41	9.62	16.84	10.57	8.45	8.07	11.83	11.98	15.73	15.35	8.48	9.18
CaO	14.44	14.52	8.49	12.44	12.90	12.41	17.33	17.78	24.07	24.15	15.34	16.32
Na ₂ O	6.20	6.08	3.58	5.43	7.22	7.16	4.73	4.51	0.70	0.55	4.98	4.21
K ₂ O	bd	bd	0.21	0.07	bd	bd	bd	bd	bd	bd	bd	bd
Cr ₂ O ₃	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Total	100.45	101.44	98.34	100.90	101.13	100.58	100.91	102.30	100.38	99.94	99.49	98.94
Si	2.00	1.99	1.97	1.98	1.99	2.00	1.98	1.98	1.98	1.97	1.89	1.89
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Al	0.40	0.40	0.32	0.41	0.50	0.52	0.34	0.33	0.07	0.08	0.48	0.43
Fe ²⁺	0.09	0.08	0.20	0.16	0.08	0.09	0.04	0.05	0.10	0.10	0.15	0.16
Fe ³⁺ ^a	0.02	0.03	0.00	0.01	0.01	0.00	0.02	0.02	0.01	0.02	0.06	0.07
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.50	0.51	0.91	0.57	0.44	0.43	0.63	0.63	0.85	0.84	0.46	0.50
Ca	0.55	0.56	0.33	0.48	0.49	0.47	0.66	0.68	0.94	0.95	0.60	0.64
Na	0.43	0.42	0.25	0.30	0.49	0.49	0.33	0.31	0.05	0.04	0.35	0.30
K	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\delta^{18}\text{O}^*$	2.8 ± 0.1	2.9 ± 0.1	3.5 ± 0.3	3.6 ± 0.3	9.1 ± 0.5	9.2 ± 0.5	0.2 ± 0.2	0.1 ± 0.2	4.1 ± 0.2	4.1 ± 0.2	3.8 ± 0.1	4.0 ± 0.1
<i>n</i>	5	2	2	2	4	4	5	5	5	5	5	4
Bulk $\delta^{18}\text{O}^b$							-0.02 ± 0.18		4.38 ± 0.31		3.69 ± 0.48	

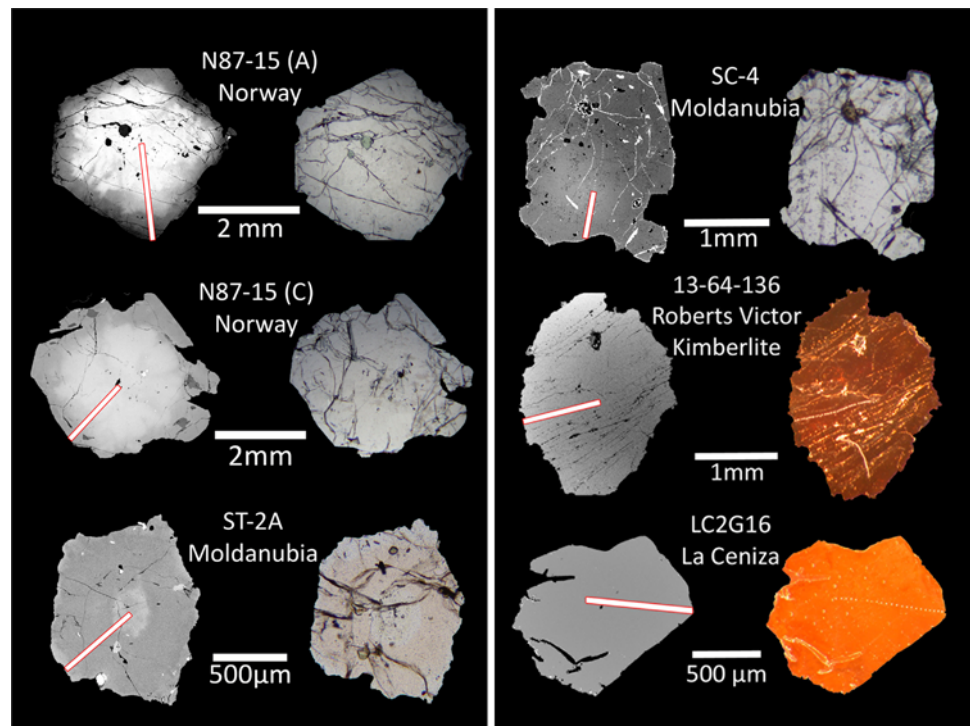
All values are averages of 2–5 grains per sample

* SIMS average values (‰, VSMOW) ± 2SD

bd, below detection limit

^a Fe³⁺ calculated based on 6 oxygen and 4 cations^b Analyzed using laser fluorination (‰, VSMOW). EPMA Point 1: Center of the grain, EPMA Point 2: ~50 μm away from grain rim

Fig. 1 A selection of 3 orogenic and 3 xenocryst eclogite garnets analyzed by SIMS and EPMA. SIMS traverses are marked in *red* and *white*. EPMA traverses are near SIMS traverses but not overlapping. Images are paired: BSE images are on *left*, photomicrograph or transmitted light images (for kimberlite xenolith *red–orange* garnets) are on *right*. Images of all analyzed garnets are in Online Resource 1



Electron probe microanalysis (EPMA)

EPMA by wavelength dispersive spectrometry was performed with a 5-spectrometer CAMECA SX51 electron microprobe in the Department of Geoscience, University of Wisconsin-Madison. Major and minor element (Si, Ti, Al, Cr, Fe, Mn, Mg, and Ca) concentrations were determined for all garnets. Coexisting clinopyroxenes were also analyzed (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, and Na).

For garnets, data were collected in automated linear traverses from core to rim at even increments of 10–30 μ (Fig. 1, Online Resource 1). In the La Ceniza xenocrysts, traverses with a length of ~ 1 mm were made from the rim to the interior, but the garnets are fragments and cores are not identified (see Fig. 1). For clinopyroxenes, EPMA spot analyses were taken in the cores and within ~ 50 μ m of the rims. From each sample, 2–5 clinopyroxene grains were analyzed. For both garnets and clinopyroxenes, Fe^{2+} and Fe^{3+} were calculated based on stoichiometry and assuming no vacancies.

SIMS analysis of $\delta^{18}\text{O}$

Garnets and clinopyroxenes were analyzed in situ in polished, 1" round thin sections or in epoxy mounts. UWG-2 garnet standard and UWQ-1 quartz standard ($\delta^{18}\text{O} = 12.33$ ‰, Kelly et al. 2007) were top-mounted directly into thin sections or into billets prior to thin sectioning. Standards were placed next to the garnet of interest

and within 5 mm of the center of the mount (Valley and Kita 2009).

Oxygen isotope ratios were measured in six separate SIMS sessions from July 2010 to October 2011 using a CAMECA ims-1280 ion microprobe at the WiscSIMS Lab, Department of Geoscience, UW-Madison (procedures described by Kita et al. 2009; Valley and Kita 2009; Page et al. 2010). The ims-1280 measures $\delta^{18}\text{O}$ with a spot-to-spot precision of 0.3 ‰ (2SD). In these sessions, pit size was approximately 10 μ m in diameter and 1 μ m deep. Garnet analysis is carefully calibrated using several garnet standards (Page et al. 2010, listed in Online Resource 1), which bracket the chemical compositions of the sample garnets.

Values of $\delta^{18}\text{O}$ for sample garnets were analyzed from SIMS pits placed evenly from core to rim along the same traverse as the EPMA analysis (Figs. 1, 2). Analyses of 10–12 individual spots were bracketed by 4 to 5 analyses of UWG-2, before and after each group of sample data, where the analytical precision is estimated as the spot-to-spot reproducibility of the homogeneous standard for each bracket (see Valley and Kita 2009 and Page et al. 2010 for further explanation). The external precision is determined to be the “best metric” for error estimation by Page et al. (2010). The average analytical precision is ± 0.26 ‰ (2SD) with precision varying from ± 0.08 to 0.53 ‰ for individual brackets. Accuracy associated with garnet analysis by this approach is estimated at 0.5 ‰ (Page et al. 2010). Raw $\delta^{18}\text{O}$ values were corrected to VSMOW using UWG-

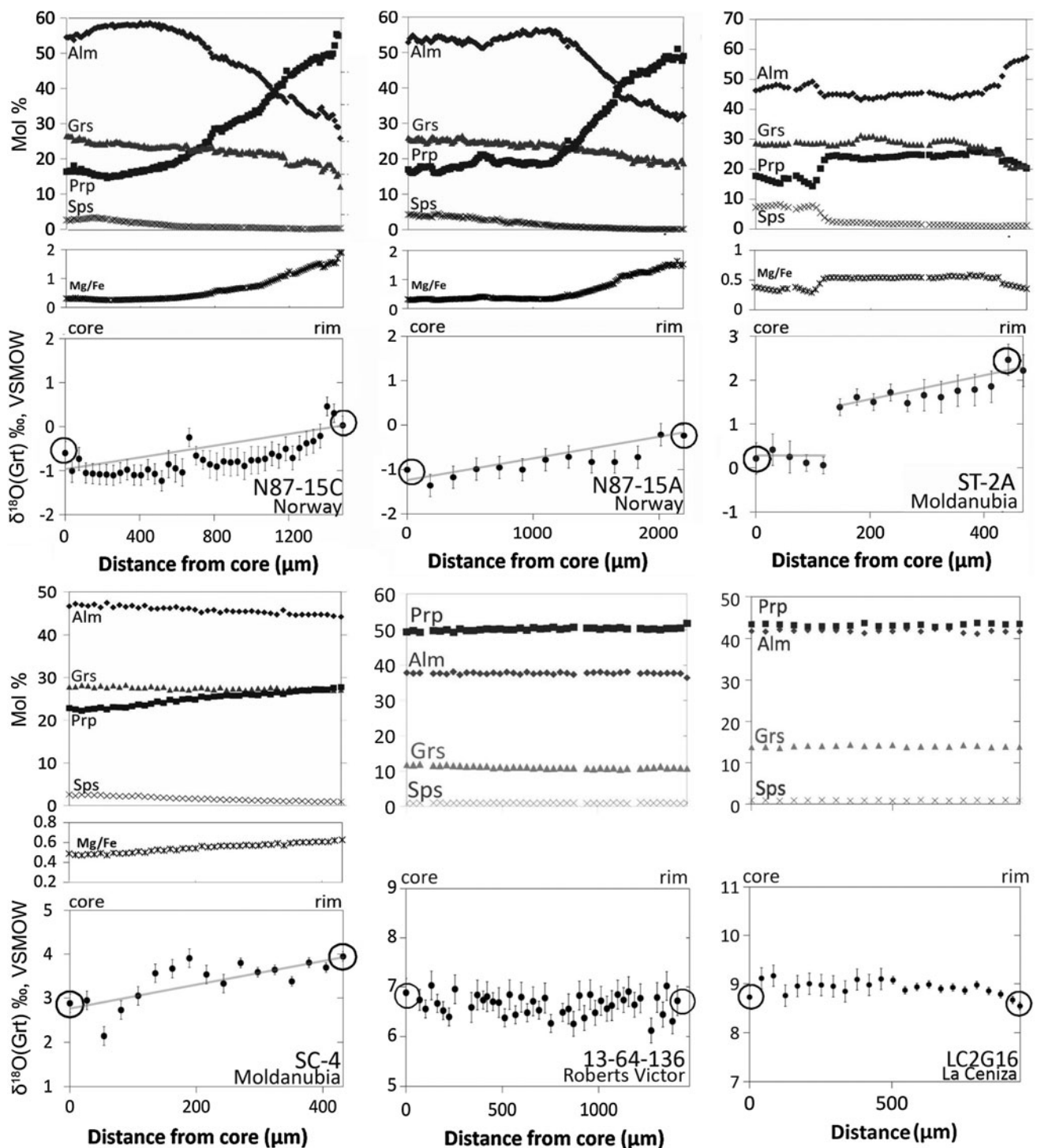


Fig. 2 Coupled major element and $\delta^{18}\text{O}$ zoning profiles from six of 19 eclogite garnets measured at WiscSIMS. All other profiles are in Online Resource 1. All profiles are from core to rim, except for La Ceniza garnet xenocrysts due to their fragmental nature. Gray lines

indicate $\delta^{18}\text{O}$ trends in garnets from orogenic eclogites. Note that the scale changes from plot to plot. See text for explanation. Abbreviations: Alm almandine, Grs grossular; Prp pyrope, Sps spessartine

2 standard brackets and a working curve for garnet composition (Page et al. 2010). Clinopyroxene $\delta^{18}\text{O}$ values were measured in cores and near rims of several (2–5) grains per sample and corrected to VSMOW using UWQ-1

as a running standard calibrated against a linear working curve for diopside (ADK-6, $\delta^{18}\text{O} = 24.14$ ‰ VSMOW, Edwards and Valley 1998) and a new jadeite standard, Jd1 ($\delta^{18}\text{O} = 8.73$ ‰ VSMOW, Online Resource 1).

Results

Coupled $\delta^{18}\text{O}$ and cation zoning profiles

A total of 19 individual garnet $\delta^{18}\text{O}$ zoning profiles were measured in situ by SIMS and correlated with major element composition measured by electron microprobe (Fig. 2 and Online Resource 1). Representative major element analyses for garnet (Table 2) are associated with individual oxygen isotope values at the core and rim of each profile, as indicated by the circled data points in Fig. 2. Twelve profiles are from garnets of orogenic eclogites and seven are from eclogite xenolith garnets. Fig. 2 displays four

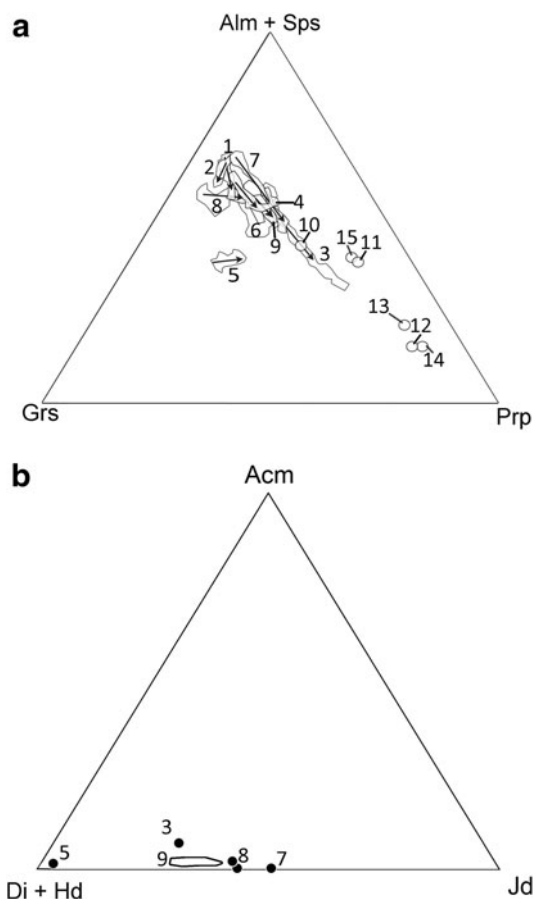


Fig. 3 Ternary diagrams showing the compositions of garnet from eclogites (**a**) and clinopyroxene (**b**). In **a**, each numbered field represents the compositional variation of a garnet grain from core to rim. Arrows point toward the rim for those garnets with simple compositional trends (Table 2). In **b**, average clinopyroxene compositions are plotted from values in Table 3. Samples are as follows: 1, FB26; 2, FB23; 3, N87-15A and N87-15C; 4, PC-2; 5, SP-1; 6, ST-2A; 7, TR00-27; 8, 89GM24A and MZ-1; SC-4 (9); 13-64-122 (10); 13-64-136 (11); LC1G8 (12); LC1G9 (13); LC2G14 (14); and LC2G16 (15). Abbreviations: *Alm* almandine, *Sps* spessartine, *Grs* grossular, *Prp* pyrope, *Acm* acmite, *Di* diopside, *Hd* hedenbergite, *Jd* jadeite

orogenic eclogite profiles and two xenolith garnet profiles; all 19 profiles can be viewed in Online Resource 1.

All analyzed garnets from orogenic eclogites are zoned with respect to $\delta^{18}\text{O}$. Most $\delta^{18}\text{O}$ profiles show a $\delta^{18}\text{O}$ (rim–core) of 1–3 ‰. The maximum variation within a single garnet is 3.7 ‰. Eight out of 12 garnets show a clear increase in $\delta^{18}\text{O}$ from the core to the rim. Two garnets (PC-2 and SP-1; Online Resource 1) decrease in $\delta^{18}\text{O}$ from core to rim, and two others [FB23(1) and FB26; Online Resource 1] have subtle variability. The majority of orogenic garnets are almandine-rich (*Alm*) with little spessartine (*Sps*) component and moderate concentrations of pyrope (*Prp*) and grossular (*Grs*) (Table 2; Figs. 2, 3a). The major element zoning of these garnets is toward more pyrope-rich rims (Fig. 3a). Clinopyroxenes that coexist with analyzed garnets from Trescolmen, Almenningen, and the Saxothuringian and Moldanubian Zones are omphacite, except for SP-1, which is sodic augite (Table 3; Fig. 3b). Following are descriptions of the laser fluorination, EPMA, and SIMS results for three of the garnets analyzed from orogenic eclogites and the seven garnets analyzed from xenoliths. The garnets investigated below demonstrate contrasting types of zoning profiles, or the lack thereof. Descriptions for garnets from other orogenic eclogites not described here are in Online Resource 1.

Western Gneiss Region, Norway: N87-15 (Almenningen)

Garnet from the Almenningen eclogite, Norway, has a bulk (laser fluorination) $\delta^{18}\text{O}$ value of -0.4 ‰ (Table 2). The two analyzed garnets, N87-15C and N87-15A (Fig. 1), were selected from different locations in the same hand sample, ~ 4 cm apart. Both garnets (Fig. 2) have similar major and minor element zoning from core to rim, which include steady decreases in *Grs* and *Sps*, and strong increases in *Prp* from ~ 16 to 50 %. In N87-15C, *Alm* decreases steadily from the core (at approximately 300–400 μm) to the rim. In N87-15A, *Alm* fluctuates slightly until a steady decrease at 1,200 μm from the core. Both garnets show large increases in the Mg/Fe ratios from 0.3 in the cores to 1.5 at the rims, demonstrating prograde mineral growth. Garnets in both samples show steady increases in $\delta^{18}\text{O}$ from ~ -1 ‰ in the cores to rim values of ~ 0 ‰ (see Fig. 2) at different resolutions.

Moldanubian Zone, Bohemian Massif, Czech Republic: ST-2A (Šachotín, Monotonous Series)

The Šachotín eclogite (Medaris et al. 1995) has a low bulk $\delta^{18}\text{O}(\text{Grt}) = 1.8$ ‰ (Table 2). The garnet selected for SIMS analysis (Figs. 1, 2) shows three zones distinguished by major element compositions, including a core with Mg/Fe

ratio of ~ 0.34 , a discontinuity at ~ 125 mm and an intermediate zone with Mg/Fe ratio of ~ 0.54 , followed by a retrograde rim at ~ 400 mm with increasing Alm and decreasing Prp and Grs. The in situ SIMS $\delta^{18}\text{O}$ zoning correlates directly with the major element-zoning pattern. From the core to ~ 125 μm , $\delta^{18}\text{O}$ is homogenous at ~ 0.2 ‰. A sharp discontinuity follows, where $\delta^{18}\text{O}$ increases to ~ 1.4 ‰. From 150 μm to the rim, $\delta^{18}\text{O}$ increases steadily to a value of 2.2 ‰ (see Online Resource 2).

Roberts Victor kimberlite: 13-64-122 and 13-64-136 (eclogite xenoliths)

Garnets from two Roberts Victor eclogite xenoliths (Schulze et al. 2000) have relatively homogenous compositions of major elements and $\delta^{18}\text{O}$ from core to rim. Two separate garnets from xenolith 13-64-122 (Online Resource 1) have a chemical composition of $\text{Alm}_{39}\text{Prp}_{38}\text{Grs}_{22}\text{Sps}_1$ and $\delta^{18}\text{O}$ of $\sim 7.5 \pm 0.3$ ‰ (2SD). Garnet from xenolith 13-64-136 (Fig. 2) has a composition of $\text{Alm}_{38}\text{Prp}_{50}\text{Grs}_{11}\text{Sps}_1$ and an irregular, small variation of $\delta^{18}\text{O}$, with an average value of 6.7 ± 0.4 ‰ (see Online Resource 2).

La Ceniza kimberlite: Eclogitic garnet xenocrysts

Four garnet xenocrysts from the La Ceniza kimberlite were analyzed. Three have no major element zoning and a range in composition of $\text{Alm}_{15-20}\text{Prp}_{70-85}\text{Grs}_{9-11}\text{Sps}_1$ (Online Resource 1, Fig. 2). These garnets have unzoned $\delta^{18}\text{O}$ values, with traverse averages of 5.2, 7.8, and 5.9 ‰, as determined by SIMS (see Online Resource 2). A fourth garnet, LC2G16, is different from the other three, having a major element composition of $\text{Alm}_{43}\text{Prp}_{43}\text{Grs}_{12}\text{Sps}_2$. For La Ceniza, it has the highest average $\delta^{18}\text{O}$ (8.8 ‰ by SIMS). This garnet (Fig. 2) has no major element zoning. Oxygen isotope ratios in Fig. 2 show a flat profile (within uncertainty) at ~ 8.9 ‰ from the core to ~ 850 μm , after which there is a gradual decrease of 0.5 ‰ over the last 100 μm to the garnet rim. The grain-to-grain variability in $\delta^{18}\text{O}$ values for these garnets agrees with that found for bulk mineral laser fluorination analyses by Schulze et al. (2003b).

Clinopyroxene–garnet fractionation of $\delta^{18}\text{O}$

Oxygen isotope values (SIMS) for coexisting garnet and clinopyroxene are listed in Tables 2 and 3. To determine whether garnets and clinopyroxenes are in oxygen isotope equilibrium, $\delta^{18}\text{O}(\text{Cpx-Grt})$ values were estimated for equilibrium fractionation (Valley 2003), where $\delta^{18}\text{O}$ is the difference, $\delta^{18}\text{O}(\text{Cpx}) - \delta^{18}\text{O}(\text{Grt})$. Equilibrium fractionation estimates of $\delta^{18}\text{O}(\text{omphacite-garnet})$ are 0.17 ‰ at

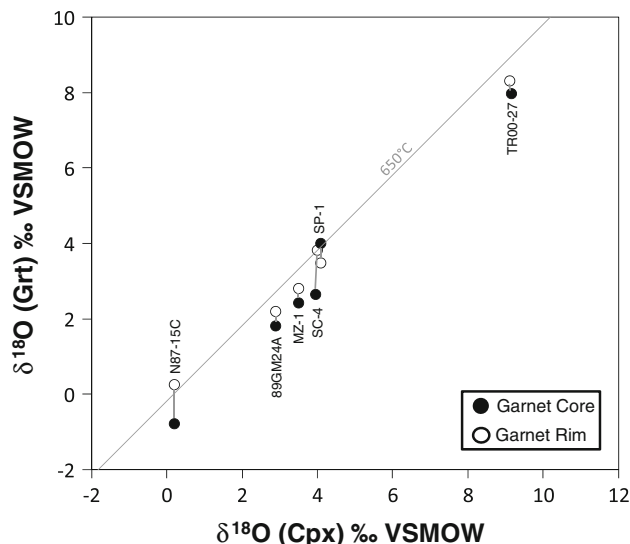


Fig. 4 Comparison of SIMS $\delta^{18}\text{O}$ for clinopyroxene with the range of SIMS $\delta^{18}\text{O}$ values in garnet, plotted as averaged rim and core values (open and filled circles, respectively). Clinopyroxene cores and rims are homogeneous and are plotted at a single value. The isopleths for $\delta^{18}\text{O}(\text{omphacite-garnet}) = 0.17$ ‰ at 650 °C are plotted for the compositions of garnet = $\text{Alm}_{60}\text{Prp}_{20}\text{Grs}_{20}$ and clinopyroxene = $\text{Di}_{50}\text{Jd}_{50}$ (see text)

650 °C for the compositions of garnet = $\text{Alm}_{60}\text{Prp}_{20}\text{Grs}_{20}$ and clinopyroxene = $\text{Di}_{50}\text{Jd}_{50}$. The estimates are interpolated from end-member garnet and clinopyroxene compositions (Kieffer 1982; Matthews et al. 1983; Valley 2003). Fig. 4 is a plot of $\delta^{18}\text{O}$ measured in coexisting garnet and clinopyroxene. Garnet rims and cores are plotted separately; clinopyroxenes have relatively uniform $\delta^{18}\text{O}$ values and are plotted at a single value. For comparison, a line is shown for the equilibrium distribution of $\delta^{18}\text{O}$ between clinopyroxene and garnet at 650 °C [$\delta^{18}\text{O}(\text{Cpx-Grt}) = 0.17$]. With one exception, garnet cores are lower in $\delta^{18}\text{O}$ than the rims. The $\delta^{18}\text{O}$ value of clinopyroxene is similar to the rim value of coexisting garnet, with $\delta^{18}\text{O}(\text{omphacite-garnet}_{\text{rim}})$ averaging 0.5 ± 0.6 ‰ (2SD), which, within uncertainty, is consistent with high-temperature equilibration predicting that clinopyroxenes grew at the same time as garnet rims.

Discussion

The effect of diffusion on $\delta^{18}\text{O}$ zoning

Distances of intragranular oxygen diffusion can be estimated to evaluate whether diffusive exchange could cause smoothing of preexisting intramineral zoning profiles or produce zoning at rims. Distances for volume diffusion of oxygen in garnet are estimated from Equations 2.45 and 3.13 of Crank (1975) for one-dimension geometry, 50 %

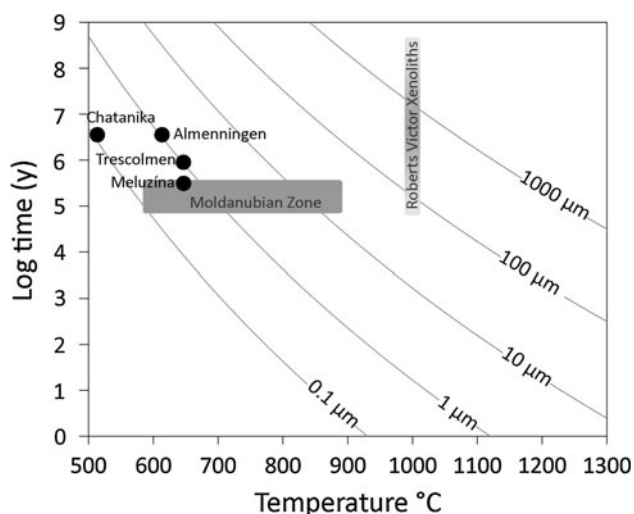


Fig. 5 Diffusion distances for oxygen in garnet plotted for temperature and time for 50 % exchange in a 1-D isothermal model (see text). A range of possible times is plotted for the Roberts Victor eclogite xenoliths

exchange, and constant temperature. These are minimum values, as further exchange could occur during slow cooling. Whereas this simplified approach could be refined (Eiler et al. 1993), the uncertainties in diffusion coefficient of garnet and thermal history of the samples do not justify more complex models. Diffusion distance is related to time for 1-D isothermal exchange by $X \approx \sqrt{Dt}$, where X is distance (cm), t is time (s), and D is the diffusion coefficient for oxygen in garnet (cm^2/s). D is calculated from

$$D = D_0 e^{\left(-\frac{E_a}{RT}\right)} \quad (1)$$

where R is the gas constant (J/mol K), T is temperature ($^{\circ}\text{K}$), and E_a is the activation energy (J/mol) (Valley 2001; Cole and Chakraborty 2001). The pre-exponential term for

oxygen in garnet, D_0 , has a value of $5.99 \times 10^{-5} \text{ cm}^2/\text{s}$ (Coghlan 1990, for hydrothermal conditions) and the activation energy, E_a , is $301,000 \pm 46,000 \text{ J/mol}$ (Coghlan 1990; Cole and Chakraborty 2001). Figure 5 displays the oxygen diffusion distances calculated for the temperature and duration of metamorphism of each sample (Table 4).

Garnets in this study from the Saxothuringian Zone, the Alps, the Western Gneiss Region, Chatanika, and three of four garnets of the Moldanubian Zone have oxygen diffusion distances of 0.1–4 μm for the duration of peak T during metamorphism (see Online Resource 1). The effects of diffusion could be greater if rocks experienced slow cooling, but still these distances are orders of magnitude shorter than the gradients measured by SIMS, suggesting that diffusive exchange was at most a minor effect in the orogenic eclogite garnets.

Infiltration of fluids during garnet growth

The estimated diffusion distances indicate that intracrystalline diffusion does not account for the $\delta^{18}\text{O}$ zoning in the zoned garnets and that the $\delta^{18}\text{O}$ zoning formed during prograde crystal growth. Thus, the changes in $\delta^{18}\text{O}(\text{Grt})$ require exchange with rocks of different composition, most likely via continuous, or in some cases, episodic infiltration of a fluid was not in equilibrium with garnet cores. For eclogites, such infiltration reasonably correlates with transport from low-pressure to high-pressure conditions during garnet growth, and the geological setting suggests that many of these garnets formed during subduction of either oceanic or continental crust. The presence of sharp gradients preserved in many of the major element-zoning profiles indicates that diffusion distances were significantly shorter than the radius of these garnets. Thus, diffusion cannot have caused core-to-rim exchange, and the increase

Table 4 Calculated diffusion distances (X), assuming peak temperature (T) and time (t) for garnets analyzed by SIMS

Sample	T (Kelvin)	Ref. #	t (y)	Ref. #	D (cm^2/s)	X (μm)
89GM24A	923	1	5×10^5	4	5.53556E-22	1
MZ-1	923	1	5×10^5	4	5.53556E-22	1
TR00-27	923	3	9×10^5	2	5.53556E-22	1
N87-15	902	5	5×10^6	6	2.22114E-22	2
ST-2A	933	7	5×10^5	8	8.42823E-22	1
PC-2	1,003	7	5×10^5	8	1.26423E-20	4
SP-1	1,003	7	5×10^5	8	1.26423E-20	4
SC-4	1,173	8	5×10^5	8	2.36403E-18	61
FB23	796	9	5×10^6	9	1.06019E-24	0.1
FB26	796	9	5×10^6	9	1.06019E-24	0.1

Diffusion coefficients and distances calculated using equations 2.45 and 3.13 of Crank (1975), see text. Diffusion data are $D_0 = 5.99 \times 10^{-5} \text{ cm}^2/\text{s}$ and $E_a = 301,000 \text{ J/mol}$ (Coghlan 1990). Time (t) is the duration of peak metamorphism. References (Ref.): (1) Klápvová et al. (1998), (2) Faryad and Chakraborty (2005), (3) Liati et al. (2009), (4) Willner et al. (2002), (5) Cuthbert et al. (2000), (6) Hacker (2007), (7) Medaris et al. (1995), (8) Medaris et al. (2006a), (9) Douglas et al. (2002)

in the Mg/Fe ratio is best explained as prograde growth zoning. The equilibrium fractionations of $\delta^{18}\text{O}$ between omphacite and garnet rims (Fig. 4) indicate that prograde fluid infiltration ended by the time garnet rims and high-pressure pyroxenes crystallized. Thus, garnets grew during prograde metamorphism coupled with a positive flux of externally derived fluids. A variety of both high and low $\delta^{18}\text{O}$ (fluids) are possible, depending on tectonic setting and associated rock types.

Garnet $\delta^{18}\text{O}$ zoning

Trescolmen, Alps

Garnet from sample TR00-27 has high bulk $\delta^{18}\text{O}(\text{Grt}) = 8.2\text{‰}$ (Wiesli 2002), and high $\delta^{18}\text{O}$ values in the garnet core (7.7‰) and rim (8.3‰). Such high values are in the range of other high $\delta^{18}\text{O}(\text{Grt})$ values of 5.3–9‰ determined by laser fluorination for Trescolmen eclogites (Wiesli et al. 2001; Wiesli 2002). Based on major and minor element analysis, Santini (1992) demonstrated a MORB-like composition for the Trescolmen eclogites. If this eclogite is metamorphosed oceanic crust, the high $\delta^{18}\text{O}$ value in the garnet core (TR00-27) is most likely inherited from altered, upper crust. In addition to an already high $\delta^{18}\text{O}$ value in the garnet core, the “saw-tooth” $\delta^{18}\text{O}$ pattern (Online Resource 1, Fig. 2) indicates oscillation of higher and lower $\delta^{18}\text{O}$ fluids that ultimately created an increased value at the rim ($T > 550\text{ °C}$). Such high $\delta^{18}\text{O}$ fluids could have exchanged with mixed fluids from high- $\delta^{18}\text{O}$ oceanic sediments and high- $\delta^{18}\text{O}$ altered basalts. The overall increase in $\delta^{18}\text{O}$ from core to rim is modest ($\sim 0.6\text{‰}$). It is thus also possible that some of the zoning in this garnet is due increasing temperature, especially in the presence of plagioclase (Kohn et al. 1993). However, garnet is not expected to grow during decreasing temperature, so the three steady decreases of $\sim 0.5\text{‰}$ each seen for the steps in TR00-27 still require fluid infiltration.

Almenningen, Western Gneiss Region, Norway

The previous range in bulk $\delta^{18}\text{O}$ values of garnet from eclogite in the Western Gneiss Region is 2.3–8‰ (Vogel and Garlick 1970; Agrinier et al. 1985). The lowest laser fluorination values of this study (-0.4‰) are the only negative values in the Western Gneiss Region and extend the range for bulk garnet analysis by almost 50%. SIMS analysis reveals even lower values in garnet cores (-1.2‰ , N87-15A; -1.0‰ , N87-15C). Oxygen isotope zoning in the garnet in Fig. 2 shows a 1‰ increase from the core to the rim, larger than predicted for a closed system, and thus indicates the exchange of garnet with a higher $\delta^{18}\text{O}$ fluid during prograde garnet growth.

To form hydrothermally altered rocks with negative $\delta^{18}\text{O}$ values such as those in the cores of the Almenningen garnets, fluids must have had $\delta^{18}\text{O} \sim 1\text{‰}$, for an infinite fluid/rock ratio, or lower values for a lower fluid/rock ratio. These results suggest infiltration of meteoric water at high temperature into rocks overlain, or in proximity to, rocks subject to precipitation, that is, subaerial continental crust. Previous studies have also concluded that some of the eclogites of the Western Gneiss Region represent mafic intrusions buried in situ within continental crust (Hacker et al. 2010; Cuthbert et al. 2000).

This interpretation of low $\delta^{18}\text{O}$ garnets from Norway is supported by studies in other UHP terranes. Negative $\delta^{18}\text{O}$ values in orogenic eclogites are reported from Dabie-Sulu and Kokchetav, where garnet values reach -10 and -4‰ , respectively (Yui et al. 1995, Masago et al. 2003). At Dabie and Kokchetav, interactions with heated meteoric water, possibly glacial melt water in a rift environment, have been postulated (Kokchetav: Masago et al. 2003; Dabie: Baker et al. 1997, Zheng et al. 2006).

The Bohemian Massif

In the Moldanubian Zone of the Czech Republic and the Saxothuringian Erzgebirge, SIMS in situ analysis confirms bulk $\delta^{18}\text{O}(\text{Grt})$ values that are low (2.4–3.0‰) (see Table 1 in Russell 2012), suggesting surface waters, but not low enough to distinguish between meteoric water and seawater. Both increases and decreases exist in the core-to-rim $\delta^{18}\text{O}$ profiles for garnets from the Bohemian Massif. For Meluzína from the Saxothuringian Zone, Klápová (1990) demonstrated that the eclogite has MORB-like geochemistry, based on major and minor elements, and Klápová et al. (1998) suggested that the eclogite formed during the subduction of a Saxothuringian ocean basin. Accordingly, the low $\delta^{18}\text{O}$ values in the cores of garnets from two samples (89GM24A and MZ-1) suggest that the protolith was altered, lower oceanic crust. The zoning formed during subduction as infiltrating fluids interacted with growing garnets.

In the Moldanubian Zone, eclogites have low $\delta^{18}\text{O}$ values and $\delta^{18}\text{O}$ zoning to both higher and lower values. Low $\delta^{18}\text{O}(\text{Grt})$ of $\sim 0.2\text{‰}$ also exists in the core of garnet ST-2A (Fig. 2). Other garnets from this region have core $\delta^{18}\text{O}$ values between 1.6 and 3‰, including sample SC-4 (Medaris et al. 2006b) that also has well-developed oxygen isotope zoning (Fig. 2) These low $\delta^{18}\text{O}$ values in garnet cores are inherited from the interaction of the protolith with heated surface water, either marine or meteoric. These protoliths either may be hydrothermally altered basalts formed at spreading centers prior to subduction or, in the case of the low $\delta^{18}\text{O}$ core of ST-2A, could represent mafic dikes in the continental crust of Saxothuringia and

Moldanubia that interacted with meteoric water prior to burial during continental collision, such as that shown at Kokchetav (Masago et al. 2003). Russell (2012) demonstrated that the low $\delta^{18}\text{O}$ Bohemian eclogites are surrounded by high $\delta^{18}\text{O}$ (Grt) crustal country rocks (6.7–10.1 ‰) perhaps implying differing metamorphic histories. The $\delta^{18}\text{O}$ zoning present in garnets from the Bohemian Massif indicates exchange of garnet cores with fluids that exchanged with either oceanic crust or surrounding, high- $\delta^{18}\text{O}$ gneisses and granulites. The zoning profiles are different for each sample from the Bohemian Massif indicating localized fluid flow and exchange. The future examination of many samples from one particular region may provide information on the exchange and flow of fluid over large areas during metamorphism.

Chatanika Eclogite

High $\delta^{18}\text{O}$ values (11.9–15.2 ‰), measured by both laser and SIMS, occur in all analyzed Chatanika garnets. Eclogite-facies hand samples contain centimeter-sized layers of calcite-bearing (~10 vol %) and metapelitic material (~40 vol %), and the high $\delta^{18}\text{O}$ values reflect a sedimentary protolith that locally is mafic and called eclogite (Brown and Forbes 1986, Douglas et al. 2002). Garnets FB23(1), FB23(2), and FB26 (Online Resource 1, Fig. 2) increase in $\delta^{18}\text{O}$ from core to rim. The proximity of marbles to these samples strongly suggests exchange with fluids from these high $\delta^{18}\text{O}$ rocks during prograde garnet growth. It is also possible that the small (0.2–0.4 ‰) core-to-rim increases reflect increasing temperatures, but as discussed for the Trescolmen garnet, decreases in $\delta^{18}\text{O}$ are difficult to explain in the absence of fluid infiltration because they would suggest garnet growth during cooling.

Eclogite garnets in kimberlite

In contrast to garnets from orogenic eclogites, garnets from Roberts Victor and La Ceniza show no $\delta^{18}\text{O}$ zoning (Fig. 2). For the garnets in Roberts Victor eclogite xenoliths, the estimated peak temperature of 1,000 °C (Jacob et al. 2003) would cause intragranular diffusion to extend 2,000 μm for oxygen in 100 Myr (Fig. 5). A possible range for high-temperature duration is shown in Fig. 5, because the age of eclogitization and mantle residence time of the xenoliths is unknown, although the protoliths are Archean (Jacob 2004). A long residence time at high-pressure/high-temperature conditions (>500 Myr, >1,000 °C) is possible (Jacob 2004), where entire garnets would have homogenized with respect to both oxygen isotopes and major elements. It is also possible that these garnets recrystallized in the mantle or that the garnets have always been homogeneous. The average $\delta^{18}\text{O}$ of the three Roberts Victor

garnets analyzed by SIMS (~7.5 ‰) is higher than the mantle value (~5–6 ‰) and is interpreted to be preserved from altered, upper oceanic crust.

A similar interpretation may apply to the garnet xenocrysts of the La Ceniza kimberlite. No mantle residence time information or peak temperature estimates exist. A residence time of several Myr at 1,000 °C within the mantle would be sufficient for diffusion to homogenize oxygen isotope profiles in the same manner as the Roberts Victor samples. It appears that garnets from kimberlite are not likely to be zoned in $\delta^{18}\text{O}$, due to their relatively high temperatures and residence times in the mantle. It is likely that homogeneity of $\delta^{18}\text{O}$, if not mantle-like, will provide a test to distinguish orogenic eclogite garnets from those brought up by mantle magmas.

Oxygen isotope thermometry and other implications

The presence of zoning in garnets from eclogite shows that in situ analysis is required for accurate oxygen isotope thermometry and that laser fluorination data for bulk garnet separates should be used with caution. For example, garnet in sample ST-2A, with the largest $\delta^{18}\text{O}$ (core-rim), has a bulk $\delta^{18}\text{O}$ value of 1.8 ‰, but SIMS analysis shows that the core value is ~0 ‰ and the rim is 2.5 ‰. This difference would bias $\delta^{18}\text{O}$ (Qtz-Grt) temperatures by ~135 °C and would obscure the fact that garnets grew over a range of temperatures and pressures. In contrast, in situ analysis of garnet and armored quartz inclusions could provide accurate temperatures for different stages of garnet growth (Strickland et al. 2011), assuming no diffusive exchange between the garnet and quartz. If combined with geochronology within a single garnet (Pollington and Baxter 2010) and thermodynamic modeling, the assemblages at each stage of the P–T–t path may be established and correlated with intragranular $\delta^{18}\text{O}$ changes in garnet.

Conclusions

Core-to-rim $\delta^{18}\text{O}$ zoning exists in garnets of this study from orogenic eclogites with bulk $\delta^{18}\text{O}$ (Grt) values outside of the common mantle garnet range (~5 to 6 ‰). In contrast, garnets from the selected eclogite xenoliths are unzoned with respect to $\delta^{18}\text{O}$, possibly due to diffusive exchange at high temperatures and long residence times in the mantle. The $\delta^{18}\text{O}$ zoning present in garnets from orogenic eclogites formed during prograde garnet growth, as indicated by core-to-rim elemental zoning in garnet. The $\delta^{18}\text{O}$ values in garnet commonly increase from core to rim and demonstrate an increasing scale of fluid-hosted exchange of eclogite with other rocks during metamorphism. The $\delta^{18}\text{O}$ values recorded in the garnet cores and

the changes in $\delta^{18}\text{O}$ from core to rim can assist in distinguishing an oceanic crust or a continental crust provenance for the eclogite in question. Such zoning profiles are also a possible tool for examining large-scale fluid histories in high-pressure regions. In situ analysis of garnets and mineral inclusions such as quartz may provide accurate estimates of thermal history that are precluded by bulk analysis of zoned minerals.

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