

Massive Fluid Influx beneath the Colorado Plateau (USA) Related to Slab Removal and Diatreme Emplacement: Evidence from Oxygen Isotope Zoning in Eclogite Xenoliths

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ABSTRACT

The Colorado Plateau has undergone as much as 1.8 km of uplift over the past 80 Myr, but never underwent the pervasive deformation common in the neighboring tectonic provinces of the western USA. To understand the source, timing and distribution of mantle hydration, and its role in plateau uplift, garnets from four eclogite xenoliths of the Moses Rock diatreme (Navajo Volcanic Field, Utah, USA) were analyzed *in situ* for $\delta^{18}\text{O}$ by secondary ion mass spectrometry. These garnets have the largest reported intra-crystalline oxygen isotope zoning to date in mantle-derived xenoliths with core-to-rim variations of as much as 3‰. All samples have core $\delta^{18}\text{O}$ values greater than that of the pristine mantle (~ 5.3 ‰, mantle garnet as derived from mantle zircon in earlier work) consistent with an altered upper oceanic crust protolith. Oxygen isotope ratios decrease from core to rim, recording interaction with a low- $\delta^{18}\text{O}$ fluid at high temperature, probably derived from serpentinite in the foundering Farallon slab. All zoned samples converge at a $\delta^{18}\text{O}$ value of ~ 6 ‰, regardless of core composition, suggesting that fluid infiltration was widely distributed. Constraints on the timing of this fluid influx, relative to diatreme emplacement, can be gained from diffusion modeling of major element zoning in garnet. Modeling using best estimates of peak metamorphic conditions (620 °C, 3.7 GPa) yields durations of <200 kyr, suggesting that fluid influx and diatreme emplacement were temporally linked. These eclogite xenoliths from the Colorado Plateau record extensive fluid influx, pointing to complex hydration–dehydration processes related to flat-slab subduction and foundering of the Farallon plate. Extensive hydration of the lithospheric mantle during this fluid influx may have contributed to buoyancy-driven uplift of the Colorado Plateau and melt-free emplacement of Navajo Volcanic Field diatremes.

Key words: eclogite; oxygen isotopes; SIMS; xenolith; garnet; Colorado Plateau

INTRODUCTION

Recent work has suggested that the uplift of the Colorado Plateau and other undeformed continental regions in the western USA was driven, at least in part, by the buoyancy of a hydrated lithosphere (e.g. Humphreys *et al.*, 2003; Jones *et al.*, 2015; Schulze

et al., 2015). Abundant evidence for this hydration can be found in the hydrated mantle xenoliths of the Navajo Volcanic Field. Schulze *et al.* (2015) presented geochronological evidence in eclogite xenoliths for a widespread fluid influx beneath the Colorado Plateau at ~ 28 Ma, calling this event the ‘Great Hydration’ and

arguing that this fluid pulse could have serpentinized a significant portion of the underlying plateau lithosphere. If uplift was driven by such a widespread ‘Great Hydration’ then we could expect to find further geochemical evidence of this fluid pulse in these and other xenoliths. This could provide information about the source, composition, distribution and timing of the fluid infiltration, and its tectonic framework. Whereas a number of previous studies have focused on establishing the age and pressure–temperature conditions of the various xenoliths, evidence for mantle metasomatism, and the generation of unusual lithologies (e.g. [Smith & Griffin, 2005](#); [Smith, 2010](#); [Schulze *et al.*, 2014](#)), only a single study has focused on the source of the infiltrating fluid(s) ([Marshall *et al.*, 2017](#)), and the timing and relationship to diatreme emplacement remain largely unconstrained. To study the source, timing and distribution of fluid beneath the Colorado Plateau during uplift, four eclogite xenoliths were selected for *in situ* oxygen isotope analysis and diffusion modeling of major element zoning in garnet. These xenoliths are thought to have been tectonically eroded, transported and underplated beneath the Colorado Plateau by the shallowly subducting Farallon slab, making them a potential record of the subduction-related hydration of the sub-plateau lithospheric mantle ([Smith, 2010, 2013](#)).

In situ analysis of oxygen isotope ratios in garnet has been particularly successful in identifying and differentiating fluid sources in eclogites (e.g. [Errico *et al.*, 2013](#); [Russell *et al.*, 2013](#); [Page *et al.*, 2014](#); [Rubatto & Angiboust, 2015](#)). Previous bulk measurements of oxygen isotope compositions of xenoliths from the Colorado Plateau and neighboring Rio Grande Rift preserve evidence of interaction with subducted material ([Smith, 1995](#); [Smith *et al.*, 2004](#); [Perkins *et al.*, 2006](#); [Marshall *et al.*, 2017](#)), but improvements in microanalytical techniques offer the possibility of accessing a more detailed fluid history recorded in intra-mineral isotopic zoning (e.g. [Kita *et al.*, 2009](#); [Valley & Kita, 2009](#); [Page *et al.*, 2010](#); [Ickert & Stern, 2013](#)). Concentric zoning records sequential snapshots of the mineral growth environment, placing isotopic compositions in a relative chronology, and illuminating evolving or abruptly changing fluid compositions.

The timing of transient processes (e.g. fluid infiltration) can be constrained at very short timescales (<1 Myr) and directly connected to chemical information preserved in zoning by examining diffusion profiles of major elements in garnet (e.g. [Jollands *et al.*, 2018](#); [Broadwell *et al.*, 2019](#)). The eclogite xenoliths from the Navajo Volcanic Field of the Colorado Plateau are particularly well-suited for this method as they are notable for their low temperatures of formation (e.g. [Usui *et al.*, 2003](#); [Hernández-Urbe & Palin, 2019](#)). At these temperatures, intra-crystalline diffusive length-scales are small relative to zone widths, meaning that zoning can generally be expected to survive through peak metamorphism and exhumation for reasonable residence times (e.g. [Vielzeuf *et al.*, 2005b](#); [Page *et al.*, 2010, 2014](#)).

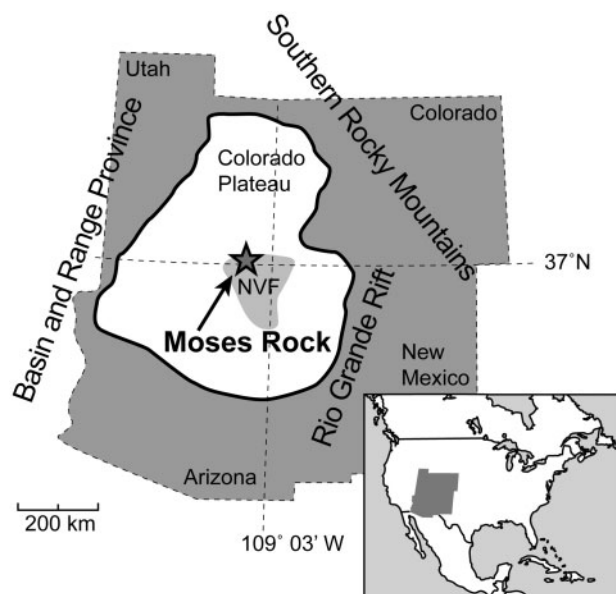


Fig. 1. A map of the southwestern USA showing the location of Moses Rock in relation to the Colorado Plateau and Navajo Volcanic Field (NVF). Although uplifted ~1.8 km, the Colorado Plateau remains largely undeformed relative to the neighboring tectonic provinces (Basin and Range, Rio Grande Rift and Rocky Mountains; modified from [Schulze *et al.*, 2015](#)).

Preserved diffusion profiles can be modeled to calculate the timing of garnet growth relative to diatreme emplacement. In this study, we use secondary ion mass spectrometry (SIMS) to analyze oxygen isotope ratios *in situ* at the ~10 μm scale in garnet and couple these measurements with diffusion modeling of divalent cations to understand the source, timing and distribution of fluid infiltration in the Colorado Plateau lithospheric mantle.

GEOLOGICAL SETTING

The four eclogite xenoliths analyzed in this study are all from the Moses Rock diatreme, part of the Navajo Volcanic Field, in the Colorado Plateau ([Fig. 1](#)). The Colorado Plateau has been uplifted ~1.8 km over the last 80 Myr; however, the temporal distribution of this uplift is poorly understood (e.g. [Sahagian *et al.*, 2002](#); [Flowers *et al.*, 2008](#); [Liu & Gurnis, 2010](#)). Although the plateau was uplifted, its interior remained relatively undeformed during the Sevier–Laramide orogeny and Basin and Range extension responsible for the extensive deformation of the neighboring Rio Grande Rift, Rocky Mountains and Basin and Range tectonic provinces (e.g. [McGetchin *et al.*, 1977](#); [Humphreys *et al.*, 2003](#); [Flowers *et al.*, 2008](#); [Liu & Gurnis, 2010](#)). During a portion of the 80 Myr period of uplift, the Farallon slab was shallowly subducting beneath the plateau, resulting in eastward migration of arc volcanism and hydration of the overlying lithosphere by fluids released by the slab during dehydration (e.g. [Dickinson & Snyder, 1978](#);

Lipman, 1992; Smith *et al.*, 1999; Saleeby, 2003; Dickinson, 2004).

The Navajo Volcanic Field (NVF) is at the center of the Colorado Plateau and comprises potassic mafic minettes and serpentinite diatremes emplaced between 19 and 32 Ma (Fig. 1; e.g. Naeser, 1971; Helmstaedt & Doig, 1975; Roden *et al.*, 1979; Laughlin *et al.*, 1986; Nowell, 1993; Smith *et al.*, 2004), concurrent with interpreted slab removal between ~20 and 40 Ma (e.g. Coney & Reynolds, 1977; Humphreys, 1995, 2009; Humphreys *et al.*, 2003; Cather *et al.*, 2008; Levander *et al.*, 2011). The diatremes are composed of serpentinized ultramafic microbreccia (SUM), and were emplaced without a melt component as SUM–gas mixtures (McGetchin & Silver, 1970, 1972; Naeser, 1971; Roden *et al.*, 1979; Roden, 1981). In addition to the SUM matrix, these diatremes contain crustal fragments sampled along the emplacement path and minor (<1%) quantities of mantle xenoliths and xenocrysts (McGetchin & Silver, 1970, 1972; Roden, 1981). These mantle-derived materials include discrete grains of pyrope, diopside and forsterite, and xenoliths of garnet and spinel peridotites, pyroxenites, garnetites and eclogites, many of which show textural and chemical evidence of extensive fluid–rock interaction (e.g. McGetchin *et al.*, 1977; Helmstaedt & Schulze, 1988, 1991; Smith *et al.*, 2004; Smith & Griffin, 2005; Smith, 2013; Schulze *et al.*, 2014).

Although the catalyst for diatreme emplacement is still unclear, Smith (2010) identified evidence in peridotite xenoliths for a short-lived (hundreds of years) thermal pulse that must have occurred immediately prior to diatreme emplacement. He attributed this thermal pulse to minette intrusion, which triggered massive devolatilization of hydrated mantle and diatreme emplacement (Smith & Levy, 1976; Smith, 2010). Pre-existing structural weaknesses may have played a role in diatreme emplacement as well, as diatremes are spatially associated with monoclines inferred to be reactivated Proterozoic shear zones (McGetchin *et al.*, 1977; Davis & Bump, 2009; Smith, 2010). Current estimates for the pressure and temperature of the diatreme source based on thermobarometry of xenoliths and discrete mineral grains suggest pressures greater than 2.4 GPa and temperatures of at least 470 °C (e.g. Smith, 2010, 2013; Schulze *et al.*, 2015). These conditions are consistent with recent peak pressure–temperature (*P–T*) estimates for eclogite xenoliths of 620 °C and 3.7 GPa from thermodynamic modeling (Hernández-Uribe & Palin, 2019), and with previous estimates from garnet–clinopyroxene–phengite thermobarometry (Helmstaedt & Schulze, 1988; Usui *et al.*, 2003; Smith *et al.*, 2004; Schulze *et al.*, 2015; Hernández-Uribe & Palin, 2019) and the presence of coesite and lawsonite (e.g. Helmstaedt & Doig, 1975; Smith & Zientek, 1979; Usui *et al.*, 2003).

The age and protolith of the eclogite xenoliths from these diatremes have been the subject of some controversy (e.g. Helmstaedt & Doig, 1975; Smith & Zientek, 1979; Wendlandt *et al.*, 1993; Usui *et al.*, 2003; Smith *et al.*, 2004).

Ages of 21–33 Ma from Sm–Nd and U–Pb dating of mineral separates and *in situ* U–Pb dating of zircons and Th–Pb dating of monazite are consistent with the timing of diatreme emplacement (Wendlandt *et al.*, 1996; Usui *et al.*, 2003; Smith *et al.*, 2004; Schulze *et al.*, 2015). Thermal ionization mass spectrometry and SIMS U–Pb dating of zircon also yielded a range of ages from 81 Ma to diatreme emplacement interpreted to record recrystallization during prograde metamorphism (Smith *et al.*, 2004; Usui *et al.*, 2006; Malik *et al.*, 2017). However, some xenoliths contain a discordant zircon population that yields Mid-Proterozoic ages (~1.5–1.7 Ga; Smith *et al.*, 2004; Malik *et al.*, 2017) similar to the Nd model ages of Wendlandt *et al.* (1993). Although it was originally thought that these eclogites were genetically related to eclogites in the Franciscan Complex, California (e.g. Helmstaedt & Doig, 1975), the Mid-Proterozoic ages are far older than the initiation of Farallon subduction (Engelbretson *et al.*, 1985; Mulcahy *et al.*, 2018) and require a source within the North American lithosphere (Smith *et al.*, 2004). Based upon prograde garnet zoning and these age constraints, the current model for these eclogites invokes tectonic erosion from the forearc lithosphere near the trench and transportation along the subduction interface to the diatreme source region (e.g. Helmstaedt & Schulze, 1991; Smith, 2010; Schulze *et al.*, 2015).

SAMPLE DESCRIPTION

Petrography

Four eclogite xenoliths were chosen for this study, and can be broadly separated into two groups: the three samples with the 12-97 prefix (12-97-11, 12-97-45, and 12-97-53), and the texturally different sample 12-83-24 (Fig. 2). All samples are dominated by omphacite and garnet and contain accessory rutile and opaque minerals. Zoisite is found only in the 12-97 samples and occurs as tabular aggregates or layers of acicular crystals. These aggregates have been interpreted as lawsonite pseudomorphs because of their tabular shape, chemical composition and the presence of relict lawsonite cores in some samples (Helmstaedt & Doig, 1975; Smith & Zientek, 1979; Usui *et al.*, 2003, 2006). Where present, foliation is defined by zoisite layers. In the 12-97 samples, garnet is porphyroblastic and shows a wide range in abundance (~5–40%) and size (0.2–3 mm) between and within individual samples. Rare atoll garnet textures with omphacite cores are found in some of the 12-97 samples (Fig. 3a and b), whereas atoll garnet textures in 12-83-24 are overgrown by new garnet (Fig. 3c). Mineralogically, Sample 12-83-24 is distinguished by the absence of zoisite and the presence of significant accessory apatite. Garnet in sample 12-83-24 occurs as laterally extensive layers up to 3 mm wide with individual porphyroblasts indistinguishable in plane- or cross-polarized light. These garnet aggregates define a moderate foliation.

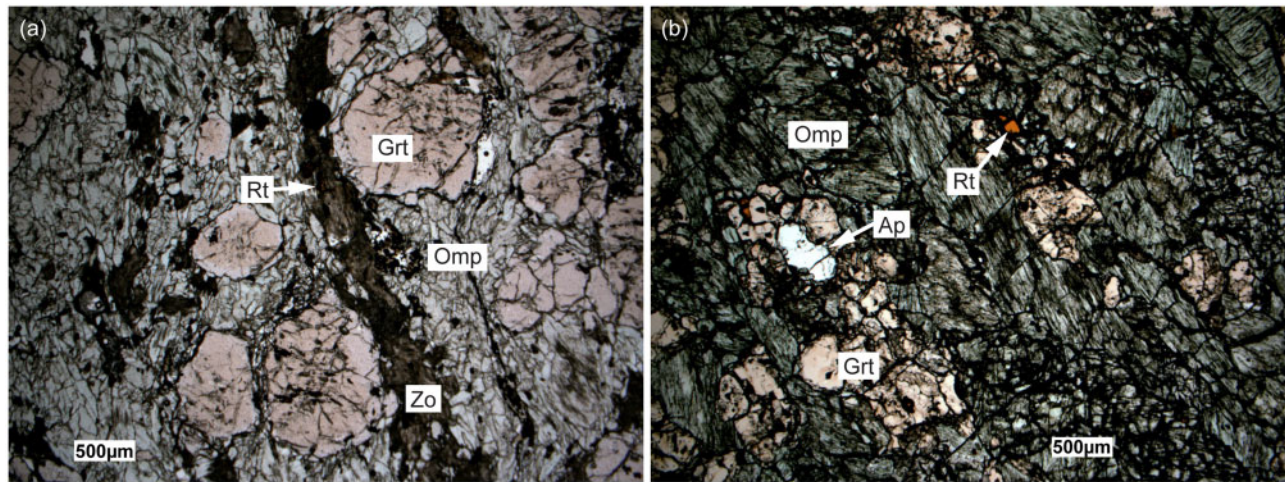


Fig. 2. Photomicrographs in plane-polarized light of (a) sample 12-97-53 and (b) sample 12-83-24 representative of the textural and mineralogical contrast between the 12-97 samples and sample 12-83-24. In 12-97-53 garnet is found as large and discrete crystals, whereas in 12-83-24 garnet forms elongate aggregates. Foliation is more pronounced in 12-97-53 and defined by zoisite, which is absent from 12-83-24. Grt, garnet; Omp, omphacite; Zo, zoisite; Rt, rutile; Ap, apatite.

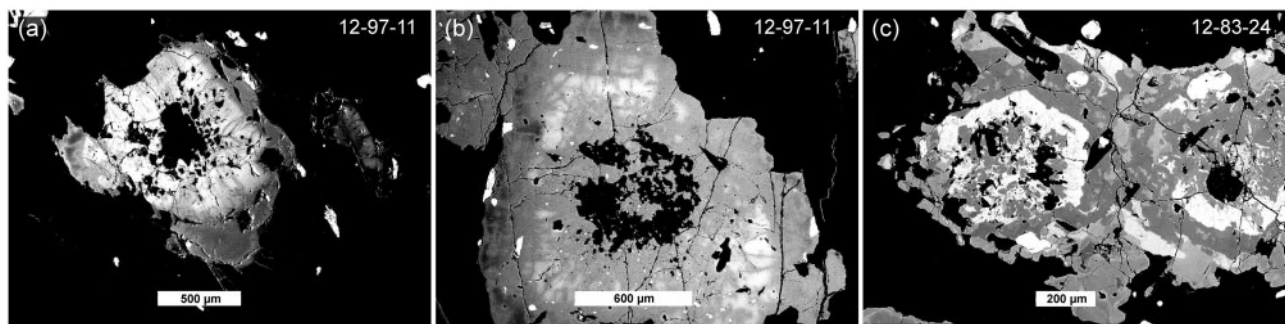


Fig. 3. High-contrast back-scattered electron images from samples 12-97-11 (a, b) and 12-83-24 (c) illustrating a variety of atoll garnet textures from Moses Rock eclogite xenoliths. Garnet cores in (a) and (b) are largely filled with omphacite (appears black). In (c), the garnet has been recrystallized, filling the euohedral atoll (bright zone) with new garnet (various grey zones).

Garnet textures

For all samples, letters following sample numbers are used to differentiate individual garnets within that sample as opposed to the sample in general. High-contrast back-scattered electron (BSE) images of garnet porphyroblasts from the 12-97 samples show irregular concentric zoning with subhedral to anhedral zone boundaries throughout (Table 1; Figs 4–6). Garnet rims are heavily embayed, such that intermediate and rim zones are discontinuous in some samples (e.g. Figs 4b and 5a). Average atomic number (Z) generally decreases from core to rim in the 12-97 samples, although mottling and incomplete low- and high- Z zones disrupt this general decrease in some garnets (e.g. 12-97-11-A, Fig. 4a). Linear features visible in BSE crosscutting core zones are present in all of the samples in this study and are interpreted as fractures healed by later garnet growth (e.g. Figs 4b, 5b, 6a and 7c).

As noted above, sample 12-83-24 is mineralogically and texturally distinct from the other samples in this study (Table 1; Figs 2b and 7a). BSE images of garnet aggregate layers from this sample exhibit extremely

complex patchwork zoning. This style of non-concentric zoning has been reported in other settings and attributed to transport-limited growth or overgrowth zoning (e.g. Yang & Rivers, 2001; Angiboust *et al.*, 2014). In garnet 12-83-24-A, the only indication of a core–rim relationship is the incomplete subhedral highest Z zone that appears to be a remnant of concentric zoning. This highest Z zone is found with a similar ring-like morphology in other garnets from this sample with some preserved euohedral faces (Fig. 3c). This remnant ring zone in all cases is overgrown (both in the core and rim) by multiple anhedral, non-concentric and discontinuous zones. Healed fractures are found in the two highest Z zones in this garnet.

ANALYTICAL METHODS

All samples were analyzed as polished thin sections. The JEOL JSM-5610 LV scanning electron microscope (SEM) at Oberlin College was used to collect BSE images to guide ion probe analyses and secondary

Table 1: Mineralogy and textural descriptions of the Moses Rock eclogite xenoliths

Sample	Mineralogy	Garnet shape	Garnet BSE texture	Cation zoning	$\delta^{18}\text{O}$ zoning (core-rim) ^a
12-97-11	Garnet + omphacite + zoisite \pm rutile \pm muscovite	subhedral	subhedral-concentric; healed fracturing	prograde	high to low
12-97-45	Garnet + omphacite \pm zoisite \pm rutile	subhedral	subhedral-concentric; healed fracturing	prograde	high to low, and homogeneous low
12-97-53	Garnet + omphacite + zoisite \pm rutile	subhedral	subhedral-concentric; healed fracturing	prograde	homogeneous high
12-83-24	Garnet + omphacite \pm rutile \pm apatite	anhedral aggregates	non-concentric; healed fracturing; remnant atoll	atoll	high atoll, low core and rim

^aHigh > $\sim 7\text{‰}$; low < $\sim 7\text{‰}$.

electron (SE) images to characterize ion probe pits post-analysis.

The CAMECA IMS 1280 ion microprobe at the WiscSIMS laboratory at the University of Wisconsin, Madison was used to analyze oxygen isotopes. Thin sections were prepared for analysis by cutting and grinding into 2.54 cm circular sections. Garnets selected for analysis were located within $\sim 5\text{mm}$ of the center of the section. After garnets were selected for analysis, UWG-2 garnet standard (Valley *et al.*, 1995) was embedded near the center of each section using epoxy and polished until coplanar with the sample. Thin section disks were gold coated before analysis. Oxygen isotope ratios were measured using the methods of Kita *et al.* (2009) and Valley & Kita (2009), with a focused beam of Cs^+ ions at a current of 1.8–2.2 nA and a spot size of $\sim 12\ \mu\text{m}$. Brackets of eight UWG-2 standard analyses were used to correct intermediate unknowns for instrumental mass fractionation (not including bias owing to different garnet cation compositions). The reproducibility of the UWG-2 standard for each bracket was assigned as the precision for intervening sample analyses; this reproducibility is a more conservative estimate of precision than the internal errors (typically 0.2‰ 2SE) based on counting statistics (Kita *et al.*, 2009). The instrumental precision based on UWG-2 reproducibility ranged from ± 0.23 to $\pm 0.62\text{‰}$ (2SD), with the majority of brackets falling close to the lower value (Supplementary Data Electronic Appendices 1 and 2; supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>). $^{16}\text{OH}/^{16}\text{O}$ was measured during each analysis to monitor for inclusions or garnet domains containing a hydrogrossular component (e.g. Wang *et al.*, 2014). All samples have similar values of $^{16}\text{OH}/^{16}\text{O}$ to the UWG-2 garnet standard, indicating similarly low OH content.

Oxygen isotope analysis of garnet by SIMS is strongly dependent on cation chemistry. Vielzeuf *et al.* (2005a) found that in garnet low in ferric iron, instrumental bias in measured oxygen isotope ratios is predominantly controlled by grossular content. The method of Page *et al.* (2010) was used to correct for the effect of compositional bias during ion microprobe analysis. Analyses of oxygen isotope ratios of eight garnet

standards that bracket the sample compositions (UWG-2, AlmSE, SpsSE, PypDM, GrsSE, Bal509, 13-63-44 and R-53) were carried out during the same analytical session and used to create a calibration curve relating bias to Ca content of garnets (Supplementary Data Electronic Appendices 1, 2 and 3). Electron microprobe analyses of cation composition were taken next to each ion microprobe pit in unknown samples and compared with the calibration curve to determine the appropriate correction for cation composition. Grossular content ranged from 10 to 36%, resulting in a matrix correction of -0.3 to $+1.0\text{‰}$ relative to UWG-2. Uncertainty in the matrix correction was assumed to be 0.5‰ (2SD) and was combined in quadrature with instrumental precision from bracketing UWG-2 analyses for total uncertainties of ± 0.55 to $\pm 0.80\text{‰}$ (2SD).

Major element analyses were carried out with the CAMECA SX100 electron microprobe at the University of Michigan, Ann Arbor. The gold coating for ion microprobe analysis was removed from the thin section disks, which were then carbon coated and analyzed using a 15 kV, 10 nA focused beam with a 20 s counting time. Natural and synthetic silicate and oxide standards were used, and data were processed using a CAMECA phi-rho-Z-type correction with oxygen calculated by stoichiometry. Ferric iron was negligible when estimated using the method of Quinn *et al.* (2016). Post-analysis SE images of each ion microprobe pit were taken to ensure that pits were inclusion free. Electron microprobe points and SIMS pits that contained inclusions or intersected cracks were excluded from this study but are included in the Supplementary Data. Pits that fell on the boundary between two $\delta^{18}\text{O}$ zones were excluded or indicated as such.

RESULTS

Garnet oxygen isotope zoning

Garnets from the 12-97 samples can be separated into two groups based upon oxygen isotope zoning (Tables 1 and 2). Garnets 12-97-11-A, 12-97-11-B and 12-97-45-A are all zoned in $\delta^{18}\text{O}$ with elevated $\delta^{18}\text{O}$ cores ($10.1 \pm 0.5\text{‰}$, $9.5 \pm 0.4\text{‰}$ and $7.3 \pm 1.2\text{‰}$, mean and 2SD, respectively) and lower $\delta^{18}\text{O}$ rims ($6.9 \pm 0.2\text{‰}$,

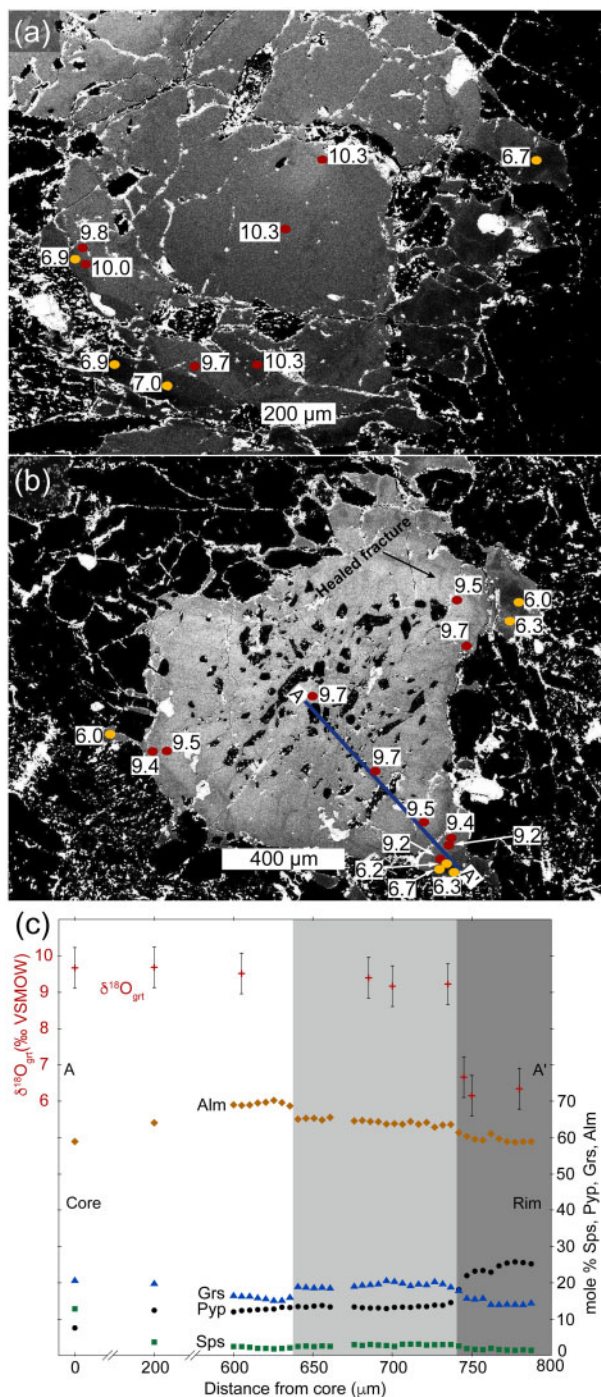


Fig. 4. Major element and oxygen isotope compositions of garnets from sample 12-97-11. High-contrast back-scattered electron images of garnets: (a) 12-97-11-A and (b) 12-97-11-B, showing high- $\delta^{18}\text{O}$ cores and low- $\delta^{18}\text{O}$ rims. These core values preserve altered upper oceanic crust protolith signatures whereas deviations at the rim record infiltration of a serpentine-derived fluid. Heterogeneity in cation composition can be seen in the bright annulus just inside the low- $\delta^{18}\text{O}$ rim in (a) relative to the prograde zoning visible in (b). Ovals mark oxygen analysis pits and are color-coded for their associated $\delta^{18}\text{O}$ zone. Pits are labeled with their associated $\delta^{18}\text{O}$ value. White flecks are residual gold coating. A traverse for cation composition and $\delta^{18}\text{O}$ from garnet 12-97-11-B is marked by a blue bar A–A' in (b) and associated analyses are plotted in (c). Shaded bands in (c) mark different grayscale zones visible in the associated BSE image (b).

$6.3 \pm 0.5\text{‰}$ and 5.8‰ , mean and 2SD, respectively) (Figs 4 and 5a, c). Garnets 12-97-45-B, 12-97-53-A and 12-97-53-B are all comparatively homogeneous in oxygen isotope composition (Figs 5b and 6). However, the $\delta^{18}\text{O}$ values in the garnets from 12-97-53 are higher than those in 12-97-45-B ($8.7 \pm 0.5\text{‰}$ compared with $6.6 \pm 0.6\text{‰}$, mean and 2SD, respectively). In the garnet from sample 12-83-24, $\delta^{18}\text{O}$ values are bimodally distributed (Fig. 7). The incomplete subhedral high-Z zone has higher $\delta^{18}\text{O}$ values and the various core and rim patchwork zones have lower $\delta^{18}\text{O}$ values ($8.9 \pm 0.6\text{‰}$ and $6.6 \pm 0.6\text{‰}$, mean and 2SD, respectively).

Garnet major element zoning

Garnets in the 12-97 samples have rims that are depleted in almandine (Alm) and enriched in pyrope (Pyp), relative to the cores. Grossular (Grs) varies little or inversely to Pyp. Traverses normal to zone boundaries (step sizes ranging from ~ 1 to $3\ \mu\text{m}$) show gradual changes in cation composition over ~ 10 – $25\ \mu\text{m}$ consistent with diffusive relaxation of an initially sharp boundary. In the garnets from samples 12-97-11 and 12-97-45, high-resolution (~ 1 – $2\ \mu\text{m}$ step size) electron microprobe traverses of healed fractures show diffusive relaxation. The major element composition of these features is most similar in composition to the garnet in the next rim-ward zone, suggesting that they grew concurrently (e.g. Figs 4b and 5a; Table 2).

As expected based upon garnet textures, cation zoning in garnet 12-83-24-A is highly variable (Table 2; Fig. 7b). Based upon major element data, four zones can be distinguished, corresponding to the four zones visible in the BSE image (Fig. 7a and 7c). Zone 1 shows distinctly lower Grs and higher Sps than the other three zones. Zones 2, 3 and 4 have similar Grs and Sps, but are distinct in Pyp and Alm.

DIFFUSION MODELING

Model setup

Traverses across zone boundaries in all 12-97 samples show small-scale gradients in major elements ($< 20\ \mu\text{m}$ in width), consistent with diffusive exchange. To estimate the timing of garnet growth relative to major tectonic events experienced by these eclogites, we created a numerical model in MATLAB to describe the diffusion of major divalent cations in garnet. This model was applied to zone boundaries and healed fractures in all 12-97 samples. Our model uses a finite difference approximation of the one-dimensional diffusion equation for a planar geometry and infinite reservoir boundary condition (Electronic Appendix 4; Crank, 1975). These conditions are justified because all traverses are short relative to garnet radii and located at a distance from grain boundaries several times the width of the diffusion profile (Fig. 8a and c). Fit of the modeled and measured profiles was assessed visually (Fig. 8b and d). Initial single-step functions in concentration were

Table 2: Representative single major element and oxygen isotopes analyses from Moses Rock eclogite xenoliths

Sample:	12-97-11								12-97-45			
	A				B				A			
Garnet:	Core	Inter.	High-Z	Rim	Core	Frac.	Inter.	Rim	Core	Frac.	Inter.	Rim
SiO ₂	38.14	38.91	38.23	37.71	37.36	38.54	38.54	39.32	36.72	38.96	39.26	39.84
TiO ₂	0.009	n.d.	n.d.	0.092	0.128	0.022	0.050	0.128	0.028	0.069	n.d.	n.d.
Al ₂ O ₃	20.32	20.98	20.94	23.24	20.74	20.58	20.92	21.03	21.17	21.38	23.07	23.28
Cr ₂ O ₃	0.032	0.039	0.047	0.055	0.045	0.024	0.028	0.081	0.048	0.018	0.046	0.021
FeO	31.36	29.39	30.08	25.35	27.00	29.72	29.65	27.77	31.20	25.33	23.08	19.27
MnO	2.28	0.52	1.40	0.59	5.81	1.41	1.31	0.67	2.65	1.02	0.54	0.37
MgO	3.07	5.76	3.39	7.49	1.95	4.30	3.38	6.68	2.62	7.51	10.59	11.39
CaO	5.86	5.26	7.24	5.67	7.38	6.21	7.07	5.30	6.76	6.93	4.40	7.11
Na ₂ O	n.d.	0.008	0.033	0.063	0.003	0.010	0.046	0.055	0.017	0.052	0.043	0.020
Total	101.06	100.87	101.36	100.26	100.41	100.83	100.99	101.04	101.20	101.26	101.03	101.30
Si	3.02	3.02	2.99	2.89	2.98	3.02	3.03	3.03	2.90	2.97	2.94	2.94
Ti	0.001	0.000	0.000	0.005	0.008	0.001	0.003	0.007	0.002	0.004	0.000	0.000
Al	1.89	1.92	1.93	2.10	1.95	1.90	1.94	1.91	1.97	1.92	2.04	2.03
Cr	0.002	0.002	0.003	0.003	0.003	0.001	0.002	0.005	0.003	0.001	0.003	0.001
Fe ²⁺	2.07	1.91	1.97	1.63	1.80	1.95	1.95	1.79	2.06	1.61	1.45	1.19
Mn	0.15	0.03	0.09	0.04	0.39	0.09	0.09	0.04	0.18	0.07	0.03	0.02
Mg	0.36	0.67	0.40	0.86	0.23	0.50	0.40	0.77	0.31	0.85	1.18	1.25
Ca	0.50	0.44	0.61	0.47	0.63	0.52	0.60	0.44	0.57	0.57	0.35	0.56
Na	0.000	0.001	0.005	0.009	0.000	0.001	0.007	0.008	0.003	0.008	0.006	0.003
% alm	67.23	62.64	64.26	54.44	58.92	63.55	64.37	58.91	66.10	52.09	47.94	39.29
% pyp	11.73	21.88	12.89	28.68	7.60	16.40	13.09	25.24	9.88	27.53	39.21	41.39
% grs	16.09	14.37	19.83	15.60	20.63	17.00	19.68	14.41	18.34	18.26	11.71	18.57
% sps	4.95	1.11	3.02	1.28	12.85	3.06	2.87	1.43	5.68	2.12	1.15	0.76
Mg#	0.15	0.26	0.17	0.35	0.11	0.21	0.17	0.30	0.13	0.35	0.45	0.51
δ ¹⁸ O	10.29	10.33	9.71	6.93	9.68	—	9.40	6.34	7.80	—	6.62	5.75
2SD	±0.65	±0.65	±0.65	±0.65	±0.56	—	±0.56	±0.56	±0.56	—	±0.56	±0.56

Sample:	12-97-45			12-97-53			B			12-83-24			
	Core	Frac.	Rim	Core	Inter.	Rim	Core	Inter.	Rim	A			
Garnet:	Core	Frac.	Rim	Core	Inter.	Rim	Core	Inter.	Rim	Core	Atoll	Rim 1	Rim 2
SiO ₂	37.21	39.10	39.05	37.91	37.72	38.03	37.95	37.60	38.25	38.96	37.66	38.13	37.72
TiO ₂	0.111	0.032	n.d.	0.148	0.156	0.090	0.185	0.239	0.006	n.d.	0.077	n.d.	0.008
Al ₂ O ₃	21.49	21.81	23.18	20.64	20.53	21.36	20.65	20.79	21.10	21.52	20.49	22.10	21.33
Cr ₂ O ₃	0.049	0.041	0.055	0.014	0.031	0.056	0.022	0.031	0.041	n.d.	0.031	0.035	n.d.
FeO	31.27	25.92	23.91	30.38	32.59	30.25	30.86	32.91	30.76	22.57	28.92	22.05	29.15
MnO	1.09	0.72	0.66	1.39	0.46	0.95	1.74	1.48	1.24	0.73	2.42	0.61	0.28
MgO	3.59	7.30	10.34	2.60	2.04	2.90	2.52	2.17	2.93	5.21	2.28	5.16	2.56
CaO	6.10	6.66	4.01	7.36	6.90	7.94	7.06	5.91	6.83	11.76	8.91	12.84	9.63
Na ₂ O	n.d.	0.030	n.d.	0.018	0.011	n.d.	0.146	0.116	n.d.	0.034	0.027	0.018	n.d.
Total	100.90	101.62	101.21	100.46	100.44	101.57	101.14	101.25	101.16	100.78	100.81	100.95	100.67
Si	2.93	2.97	2.93	3.01	3.01	2.98	3.00	2.98	3.01	2.99	2.98	2.92	2.97
Ti	0.007	0.002	0.000	0.009	0.009	0.005	0.011	0.014	0.000	0.000	0.005	0.000	0.000
Al	1.99	1.95	2.05	1.93	1.93	1.97	1.92	1.94	1.96	1.95	1.91	1.99	1.98
Cr	0.003	0.002	0.003	0.001	0.002	0.003	0.001	0.002	0.003	0.000	0.002	0.002	0.000
Fe ²⁺	2.06	1.65	1.50	2.02	2.18	1.98	2.04	2.18	2.03	1.45	1.91	1.41	1.92
Mn	0.07	0.05	0.04	0.09	0.03	0.06	0.12	0.10	0.08	0.05	0.16	0.04	0.02
Mg	0.42	0.83	1.16	0.31	0.24	0.34	0.30	0.26	0.34	0.60	0.27	0.59	0.30
Ca	0.51	0.54	0.32	0.63	0.59	0.67	0.60	0.50	0.58	0.97	0.75	1.05	0.81
Na	0.000	0.004	0.000	0.003	0.002	0.000	0.022	0.018	0.000	0.005	0.004	0.003	0.000
% alm	67.11	53.78	49.66	66.26	71.56	64.99	66.84	71.78	66.88	47.36	61.75	45.65	62.91
% pyp	13.75	27.00	38.28	10.12	7.99	11.09	9.75	8.45	11.35	19.49	8.67	19.02	9.85
% grs	16.78	17.70	10.67	20.56	19.42	21.86	19.60	16.51	19.03	31.61	24.36	34.06	26.64
% sps	2.36	1.52	1.38	3.06	1.03	2.06	3.81	3.26	2.74	1.54	5.23	1.28	0.60
Mg#	0.17	0.33	0.44	0.13	0.10	0.15	0.13	0.11	0.15	0.29	0.12	0.29	0.14
δ ¹⁸ O	6.91	—	6.41	8.50	8.58	9.03	8.60	8.29	8.68	6.65	9.16	6.30	7.27
2SD	±0.56	—	±0.56	±0.80	±0.80	±0.80	±0.80	±0.80	±0.80	±0.55	±0.55	±0.55	±0.55

inter., intermediate; frac., healed fracture; alm, almandine; pyp, pyrope; grs, grossular; sps, spessartine; n.d., not detected.

assumed unless multiple initial step functions were necessary to reproduce the topology of measured profiles (Fig. 8b). Spatial resolution of the model was at least as fine as the measured major element traverses, and time steps varied from 1200 years to 6 Myr to maintain the stability of the model. The diffusivities of divalent

cations in garnets are heavily dependent on composition (e.g. Carlson, 2006; Ganguly, 2010), so tracer diffusivities varied spatially and were recalculated at each time step in response to diffusive changes in composition. Owing to the mixed Alm–Pyp–Grs composition of these garnets, tracer diffusivities were calculated using

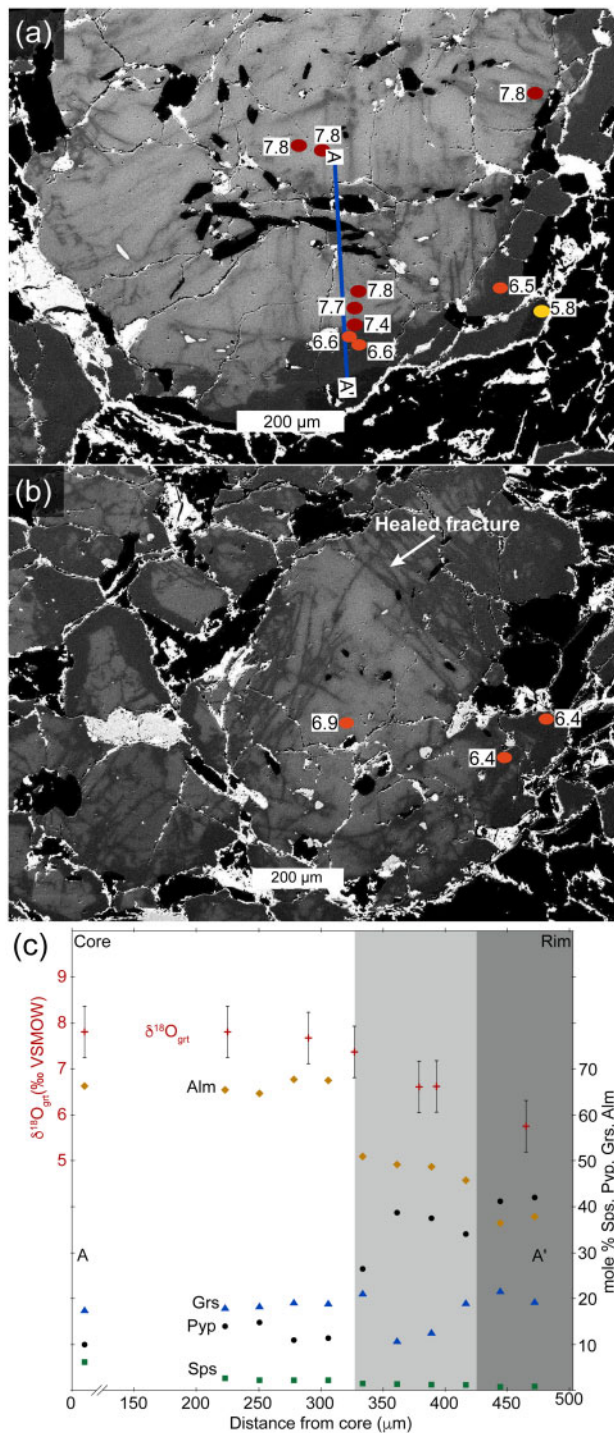


Fig. 5. Major element and oxygen isotope compositions of garnets from sample 12-97-45. High-contrast back-scattered electron images of garnets: (a) 12-97-45-A and (b) 12-97-45-B, showing the heterogeneous preservation of the lowest $\delta^{18}\text{O}$ zone. Embayed garnet rims suggest that this feature is the result of garnet resorption rather than heterogeneous distribution of the serpentinite-derived fluid. Linear features cross-cutting the cores of both (a) and (b) are fractures healed with new garnet during fluid influx. Ovals mark oxygen isotope analysis pits labeled with their associated $\delta^{18}\text{O}$ value and color-coded for their zone. Cation traverse A–A' is marked with a blue bar in (a) and associated analyses are plotted in (c). Shaded bands in (c) refer to grayscale zones visible in the associated BSE image (a).

the method of Carlson (2006), as these compositions are not well represented by experimental diffusion couples (e.g. Chakraborty & Ganguly, 1992; Ganguly *et al.*, 1998). Parameters used to calculate diffusivity (frequency factor, sensitivity to unit-cell dimension, activation energy, activation volume) were varied within uncertainties specified by Carlson (2006) as needed to maximize the fit of the model. This generally involved maximizing the diffusivity of Fe and minimizing that of Mg and Ca relative to Mn.

P–T–fO₂ inputs

Peak temperatures and thermal histories of the NVF eclogite xenoliths represent the main source of uncertainty in our model. Hernández-Uribe & Palin (2019) used thermodynamic modeling of lawsonite-bearing eclogite xenoliths from Moses Rock to calculate peak conditions of 3.7 ± 0.1 GPa and 620 ± 50 °C. These results using current thermodynamic modeling methods overlap within uncertainty all previous temperatures of Moses Rock eclogite xenoliths calculated from garnet–clinopyroxene–phengite thermobarometry (515–680 °C; Smith *et al.*, 2004; Schulze *et al.*, 2015). If consideration is extended to garnet–clinopyroxene temperatures calculated using assumed pressures >2 GPa for all NVF eclogite xenoliths, nearly all temperature estimates overlap those from thermodynamic modeling within the uncertainty (Helmstaedt & Schulze, 1988; Usui *et al.*, 2003; Smith *et al.*, 2004; Schulze *et al.*, 2015; Hernández-Uribe & Palin, 2019). Based on the agreement between traditional mineral thermometry estimates and calculated temperatures from thermodynamic modeling, the most recent pressure and temperature estimates for Moses Rock eclogite xenoliths were utilized in our diffusion models accounting for the upper and lower uncertainty bounds (Hernández-Uribe & Palin, 2019).

Limited information is available regarding the metamorphic *P–T* path of the NVF eclogites or the timing of garnet rim growth and fracture healing. For this reason, we have chosen to model diffusion at a constant temperature; however, the impact of this uncertainty is minimal based on the following geodynamic and theoretical constraints. Prolonged cooling during exhumation can be ruled out as diatreme emplacement is interpreted to have been rapid (e.g. Smith & Roden, 1981). Likewise, post-peak, pre-emplacement cooling accommodated by changes in the subduction zone thermal structure are unlikely during stable flat slab subduction. Flat slab subduction occurs under limited thermo-mechanical conditions (thick or young oceanic crust) characterized by warm geothermal gradients (e.g. Syracuse *et al.*, 2010; Huangfu *et al.*, 2016). The maintenance of flat slab subduction until contemporaneous slab foundering and diatreme emplacement (e.g. Roden *et al.*, 1979; Cather *et al.*, 2008) suggests that no changes in thermal structure occurred prior to slab foundering. These arguments suggest that no

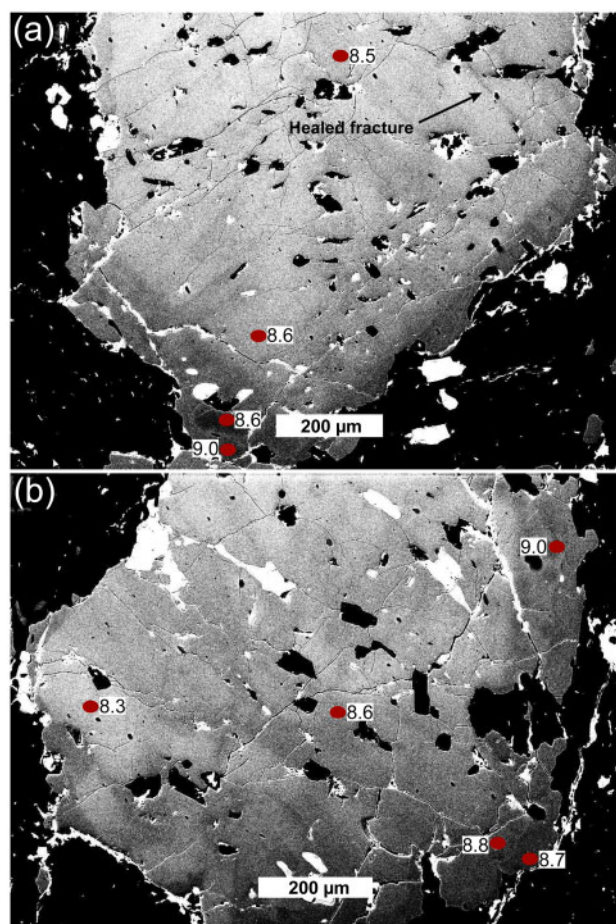


Fig. 6. Oxygen isotope compositions of garnets from sample 12-97-53. High-contrast back-scattered electron images of garnets: (a) 12-97-53-A and (b) 12-97-53-B, showing $\delta^{18}\text{O}$ homogeneity but cation zoning and healed fractures indicating changing metamorphic conditions and fluid interaction during growth. The abundance of embayments in the garnet rims suggests that lack of preservation may explain the absence of a low- $\delta^{18}\text{O}$ rim zone in this sample. Ovals mark oxygen isotope analysis pits labeled with their associated $\delta^{18}\text{O}$ values.

significant cooling (in the context of diffusion modeling) occurred post-garnet rim growth.

The effect of early garnet growth under cooler prograde conditions (heating path) cannot be ruled out but would have a minimal effect on our results. Diffusivity is exponentially dependent on temperature so diffusive distance will be dominated by the highest temperatures reached by these garnets (during peak metamorphism) even if they grew at significantly lower temperatures. In addition, the locations of our modeled chemical gradients near the rims of the garnets suggest that they represent the later portions of garnet growth and thus near-peak temperatures. Although more uncertain than peak temperature estimates owing to the challenge of establishing equilibrium relationships, garnet-clinopyroxene thermometry of garnet interiors from NVF eclogite xenoliths largely overlaps our modeled temperatures. Eight of 11 mineral pairs from the literature produce estimates greater than 570°C (Helmstaedt &

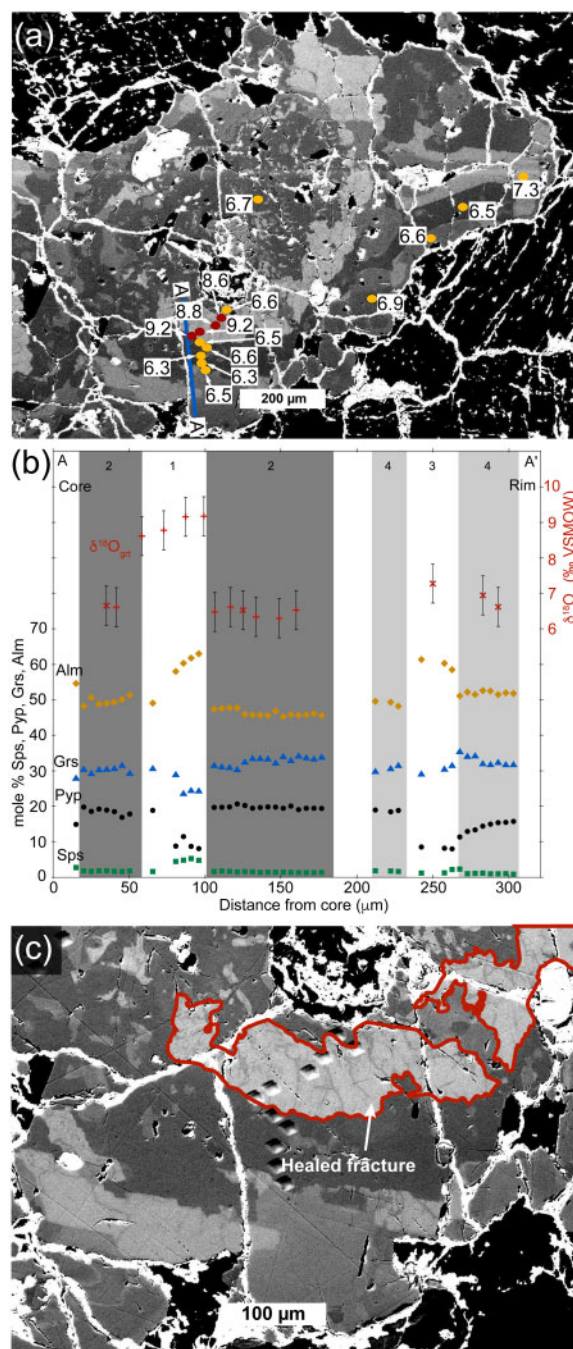


Fig. 7. Major element and oxygen isotope compositions of garnets from sample 12-83-24. (a) High-contrast back-scattered electron image of garnet 12-83-24-A showing the complex zoning characteristic of this sample. The high- $\delta^{18}\text{O}$ values in the bright zone are interpreted to represent first garnet growth with later diffusion-limited recrystallization forming the complex intergrowths in the core and rim. Ovals mark $\delta^{18}\text{O}$ analysis pits labeled with their associated $\delta^{18}\text{O}$ value and color-coded for their $\delta^{18}\text{O}$ zone. The cation traverse plotted in (b) is marked by the blue bar from A to A'. (b) Cation and $\delta^{18}\text{O}$ analyses along traverse A-A' are plotted with other $\delta^{18}\text{O}$ values assigned a position along the traverse based upon cation chemistry and marked with an 'x'. Numbers and shaded bands identify zones differentiated by oxygen isotope and cation analyses. (c) Detail of the traverse portion of (a) with the relict atoll outlined. The fine-scale, complex zoning in the later low- $\delta^{18}\text{O}$ garnet is clearly visible, as is the healed fracturing in the relict atoll.

Schulze, 1988; Schulze *et al.*, 2015). Based on this evidence, garnet rim growth significantly outside our modeled temperatures is unlikely, and would have a limited effect on our results.

The tracer diffusivity of divalent cations in garnet is dependent on the oxygen fugacity (fO_2), with variations of ~ 1.5 log units across a reasonable range of oxygen fugacities. Unfortunately, fO_2 is difficult to assess in eclogites where buffering assemblages (e.g. fayalite–magnetite–quartz) are missing or redox-sensitive element partitioning is uncalibrated. An estimate for the oxygen fugacity of a minette and associated ultramafic breccia from the Buell Park pipe (NVF) yielded values close to the fayalite–magnetite–quartz buffer using spinel–ilmenite oxybarometry (Roden *et al.*, 1982). Although it is unclear how representative this is of diatreme sources across the NVF, it was used in our model in the absence of better estimates.

DISCUSSION

Oxygen isotope compositions of eclogite xenoliths

This study reports the largest intra-crystalline $\delta^{18}O$ variation reported in mantle-derived xenoliths with variations of up to $\sim 3\%$ from core to rim across some garnets. This is in contrast to previous studies, which found little or no variation outside uncertainty in eclogitic garnets from kimberlitic xenoliths. Russell *et al.* (2013) used SIMS to analyze garnet from several kimberlitic eclogite xenoliths and reported subtle variations of ~ 0.5 and $\sim 1\%$. However, variation was not systematic, and they concluded that their garnets were largely homogeneous in oxygen isotope composition, attributing this to diffusional resetting during long residence times at mantle temperatures. Smit *et al.* (2014) analyzed garnet separates from kimberlitic eclogite xenoliths using SIMS; however, they found no significant variation in $\delta^{18}O$ and reported their results as whole crystal averages. Most recently, Riches *et al.* (2016) used SIMS to assess the record of diamond-forming metasomatism in a kimberlite-sourced eclogite xenolith. They found their garnets to be homogeneous in oxygen isotope composition and concluded that, although eclogite xenoliths may retain their oceanic crust protolith signature for long periods of time in the mantle, $\delta^{18}O$ homogeneity in garnet is probably a general characteristic of mantle eclogites. Riches *et al.* suggested that metasomatic alteration of oxygen isotope signatures in eclogite during diamond formation was unlikely, as any fluids passing through the mantle would be buffered to mantle $\delta^{18}O$ values by the inherently low fluid–rock ratio. The results of this study contrast with those of Riches *et al.*, recording and preserving evidence of interaction with a lower $\delta^{18}O$ reservoir. This suggests that in instances of low geothermal gradients, proximal and extensive fluid

production or rapid removal from mantle conditions, oxygen isotope homogeneity should not be assumed.

As has been the case in many studies of eclogite mantle xenoliths (e.g. Russell *et al.*, 2013; Smit *et al.*, 2014; Radu *et al.*, 2019), the $\delta^{18}O$ values of the eclogite xenoliths in this study (Fig. 9; Table 2) range well beyond that of mantle garnet of $5.3 \pm 0.6\%$ as derived from mantle zircon (Valley *et al.*, 1998; Page *et al.*, 2007). Oceanic basalt is elevated to $\delta^{18}O$ values above that of the pristine mantle by low-temperature alteration (e.g. Gregory & Taylor, 1981; Alt *et al.*, 1986; Eiler, 2001). This supports previous major element, Sr isotope and O isotope evidence for an oceanic crust protolith for the NVF eclogite xenoliths (e.g. Helmstaedt & Doig, 1975; Usui *et al.*, 2003; Smith *et al.*, 2004). Putlitz *et al.* (2000) found that subducted mafic rocks recrystallizing in a closed system will adopt the bulk-rock oxygen isotope signature of their protolith, supporting the interpretation that the elevated $\delta^{18}O$ values of the eclogite xenoliths in this study reflect their protolith. Oxygen isotopes also have a negligible amount ($< 0.2\%$) of temperature or pressure fractionation between garnet and the other minerals present in eclogite (Clayton *et al.*, 1975; Valley, 2003), so analyses of garnet in this study are expected to reflect the bulk- $\delta^{18}O$ of the eclogite. Based on this previous work, elevated $\delta^{18}O$ values in garnet cores from these eclogite xenoliths are interpreted to reflect the oxygen isotope signature of their altered upper oceanic crust protolith adopted during closed-system growth.

Fluid source inferred from garnet rims

The rims of some of the garnets in this study show significant differences in isotopic composition relative to their cores, indicating a change in fluid composition as opposed to P – T conditions (Fig. 9). In garnets 12-97-11-A and -B and, to a lesser extent, 12-97-45-A, $\delta^{18}O$ values decrease sharply from cores to rim values approaching that of the pristine mantle (Figs 4 and 5a, c). Because the isotopic fractionation between eclogitic minerals is minimal at the pressures and temperatures of eclogite formation (Clayton *et al.*, 1975; Valley, 2003), the only way to decrease the $\delta^{18}O$ value of the garnet is by interaction with externally derived fluids from a low- $\delta^{18}O$ reservoir at high temperatures.

In the context of these samples, there are several possible sources consistent with this low- $\delta^{18}O$ signature. Altered lower oceanic crust has $\delta^{18}O$ values lower than the mantle values but is generally the least hydrated portion of downgoing slab and thus has little fluid with which to infiltrate these eclogites (e.g. Cartwright & Barnicoat, 1999; Eiler, 2001; Hacker, 2008). This is also true of unaltered mantle wedge or slab mantle, which has an appropriate $\delta^{18}O$ value ($\sim 5.3\%$, mantle garnet derived from mantle zircon; Valley *et al.*, 1998; Page *et al.*, 2007) but is nominally anhydrous (Valley *et al.*, 1998; Page *et al.*, 2007). Serpentinite can have $\delta^{18}O$ values of ~ 1 – 8% (e.g. Cartwright &

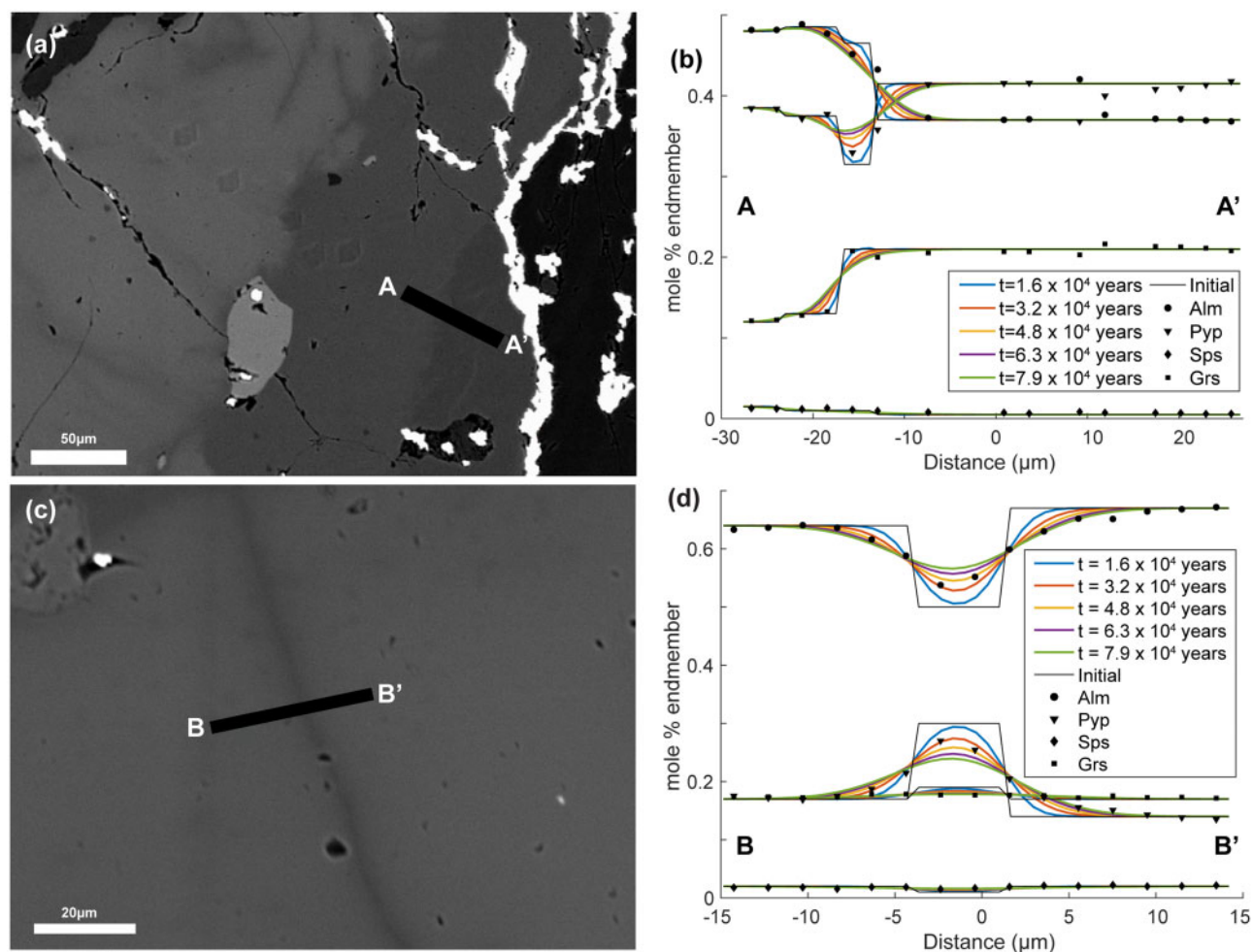


Fig. 8. Back-scattered electron images and representative multi-component diffusion model results for garnet rim (12-97-45-A outside rim) (a, b), and healed fracture (12-97-45-B fracture) (c, d) at 620 °C. In (a) and (c), black bars mark the position of measured traverses plotted in (b) and (d), respectively. Plotted lines in (b) and (d) are a range of diffusion models at 620 °C considered good fits to the measured profiles, based on visual assessment. Variability in the models in (b) close to the zone boundary is the result of a complex initial geometry. Multiple initial steps in concentration were necessary to maximize the fit of the model to the measured data. Alm, almandine; Grs, grossular; Pyp, pyrope; Sps, spessartine.

Barnicoat, 1999; Eiler, 2001; Früh-Green *et al.*, 2001; Miller *et al.*, 2001; Scambelluri *et al.*, 2004; Marshall *et al.*, 2017), and generally dehydrates at temperatures of ~600 °C, consistent with the diatreme source region (e.g. Ulmer and Trommsdorff, 1995). A serpentinite source could be in the mantle wedge (hydrated by the Farallon slab) or in the downgoing slab (hydrated along faults on the ocean floor; e.g. Ranero *et al.*, 2003).

We consider a serpentinite-derived fluid to be the most likely source of the low- $\delta^{18}\text{O}$ rims for a number of reasons. Marshall *et al.* (2017) explained low- $\delta^{18}\text{O}$ fluids recorded in hydrated peridotite NVF xenoliths with a serpentinite-derived fluid source within the Farallon slab. Serpentine dehydration inferred from textures and compositions of zoned olivine in a Cr-dunite (former low-pressure serpentinite) xenolith from the Green Knobs diatreme demonstrates that fluids were being released from serpentinite at the time of diatreme emplacement (Smith, 2010). These observations are consistent with general P - T conditions of serpentinite

dehydration, which match those of the diatreme source region (e.g. Ulmer and Trommsdorff, 1995; Usui *et al.*, 2003; Smith, 2013). Large volumes of fluid can be stored in serpentinite in the slab mantle formed during hydration along ocean floor faults (e.g. Ranero *et al.*, 2003). As the Farallon slab foundered into the asthenosphere, as is thought to have occurred between 40 and 20 Ma (Coney & Reynolds, 1977; Humphreys, 1995, 2009; Humphreys *et al.*, 2003; Cather *et al.*, 2008; Levander *et al.*, 2011), dehydrating serpentinite would have produced exceptionally large volumes of fluid. Models of diatreme emplacement also invoke dehydration of serpentinitized mantle in response to minette intrusion, offering another possible fluid production mechanism. Lastly, the volume of hydration of the Colorado Plateau mantle (i.e. SUM matrix, antigorite peridotite xenoliths, etc.) requires a large fluid volume that would be difficult to produce with a less voluminous fluid source (e.g. Hacker, 2008; Marshall *et al.*, 2017). Based on these lines of evidence, we consider a serpentinite-derived

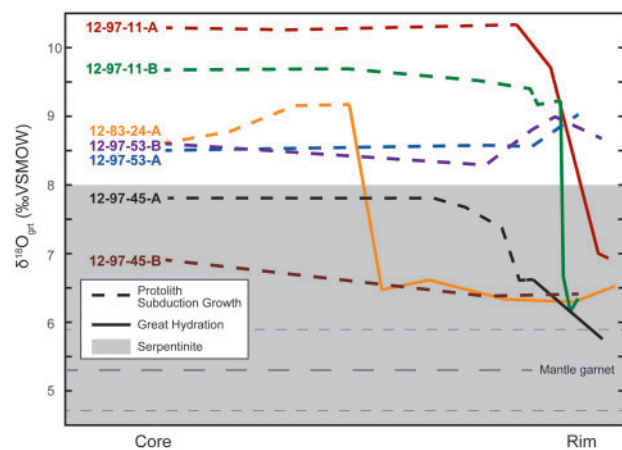


Fig. 9. Compilation of oxygen isotope profiles across garnets in this study with core-to-rim distances normalized for comparison. Low- $\delta^{18}\text{O}$ zones in all samples that preserve zoning converge at values of $\sim 6.5\text{‰}$ suggesting a shared history of fluid infiltration. Based on tectonic, trace element and stable isotope arguments, this fluid is probably derived from serpentinite in the Farallon lithospheric mantle (Marshall *et al.*, 2017). Higher $\delta^{18}\text{O}$ values in all samples are consistent with an altered oceanic crust protolith suggesting closed-system growth during prograde subduction. Mantle garnet (with 2SD uncertainty; fine dashed lines) and serpentinite (shaded region) are plotted for comparison. Analyses from sample 12-83-24 were assigned positions based on atoll and overgrowth textures.

fluid the most likely source of the low- $\delta^{18}\text{O}$ garnet rims (Fig. 9).

Sources of heterogeneity beneath the Colorado Plateau

As noted in the results, a low- $\delta^{18}\text{O}$ rim zone is preserved in only one of the analyzed garnets in sample 12-97-45 (Fig. 5). Although an intermediate zone is preserved in both garnets, this zone shows no change in isotopic composition from the core, consistent with closed-system garnet growth (Fig. 5a and b). Based upon the universal distribution of anhedral zone boundaries and crystal shapes, including embayments, and evidence of rare earth element mobilization in monazite from other eclogite xenoliths, garnet resorption is the preferred explanation for the heterogeneous spatial distribution of the low- $\delta^{18}\text{O}$ zone (e.g. Fig. 5b; Schulze *et al.*, 2015). Resorption of garnet could have been driven by the abrupt increase in temperature or decrease in pressure associated with diatreme emplacement and already invoked to explain the pseudomorphic (and in some cases incomplete; Usui *et al.*, 2003) replacement of lawsonite by acicular zoisite aggregates (Helmstaedt & Doig, 1975; Smith & Zientek, 1979; Usui *et al.*, 2003, 2006). The textural complexities of this sample, particularly in the morphology of the low- $\delta^{18}\text{O}$ rim zones, point to a complex interrelation between fluid infiltration, growth and dissolution.

In contrast to the other three samples in this study, isotopic zonation and low- $\delta^{18}\text{O}$ rims are absent from both garnets in sample 12-97-53 (Figs 6 and 9). Yet, even in the absence of isotopic evidence for fluid

interaction, healed fracturing throughout the garnet cores reflects some amount of fluid–rock interaction (Fig. 6; Table 2). The isotopic homogeneity of garnets in 12-97-53 in the presence of evident fluid interaction can be explained in several ways. The first is that fluids infiltrating this xenolith suite were sourced from multiple locations (e.g. slab serpentinite and altered oceanic crust) and those interacting with 12-97-53 were fortuitously similar in isotopic composition. This is consistent with the uniform ages but variable chemistry observed in monazite by Schulze *et al.* (2015) and attributed to heterogeneous ‘Great Hydration’ fluids, but is inconsistent with the convergence in $\delta^{18}\text{O}$ values in other samples in this study (Fig. 9). Another explanation is that healed fracturing is the result of locally derived fluid infiltration during prograde subduction, which would account for the diffuseness of the fractures relative to the other samples. Sample 12-97-53 could then have been protected from later ‘Great Hydration’ metasomatism by low permeability or a position isolated from fluid conduits. Precedent for this type of metasomatic heterogeneity is established by previous oxygen isotope studies of mantle xenoliths. Huang *et al.* (2014) observed $\delta^{18}\text{O}$ variations of $\sim 2.5\text{‰}$ at the thin section scale between different domains of an eclogite xenolith from the Roberts Victor kimberlite, South Africa. Lastly, as with 12-97-45-B, resorption of garnet during diatreme emplacement could have removed garnet rims grown during late fluid–rock interaction, leaving only the healed fractures as evidence of this fluid influx. Irregular and truncated grain and zone boundaries in these garnets are evidence that garnet resorption took place, but the lack of garnets preserving relict rims precludes a definitive statement on the origin of isotopic homogeneity in these garnets. However, sample 12-97-53 stands as a further example of the textural complexities resulting from fluid processes active beneath the Colorado Plateau.

Atoll garnet

Although atoll garnets are present in many eclogite xenoliths in the Colorado Plateau, sample 12-83-24 stands out for the presence of atoll garnet textures that are overgrown by later garnet (Fig. 3; e.g. Helmstaedt *et al.*, 1972; Smith & Zientek, 1979). Garnet 12-83-24-A is dominated by a patchwork of garnet compositions showing no typical concentric zoning patterns; however, in the core (and in the core of other garnets in this sample; Fig. 3c), a single homogeneous zone preserves an atoll-like shape. This atoll zone (1 in Fig. 7b) has a distinctly higher $\delta^{18}\text{O}$ value than the patchwork of zones that make up the rest of the garnet (Fig. 7). In the 12-97 samples where zoning is concentric, the highest $\delta^{18}\text{O}$ core represents adoption of the protolith signature and lower values in the rims record later fluid interaction. If we apply this interpretive method here, it is the incomplete atoll zone, and only concentric remnant, that represents the earliest growth in 12-83-24, and the lower

$\delta^{18}\text{O}$ patchwork core and rim zones that are later growth. These textural and $\delta^{18}\text{O}$ patterns are best explained as an atoll garnet overgrown by later garnet growth. The presence of preserved core material and euhedral outer edges in some atoll garnets from 12-83-24 (e.g. Fig. 3c) and in other studies is consistent with formation by initial skeletal growth of garnet (Smith & Zientek, 1979; Robyr *et al.*, 2014). The presence of healed fracturing in the preserved atoll suggests that fluid played a role in the later overgrowth of the patchwork rim and core garnet (Fig. 7c). The process by which the later patchwork zones grew is still unclear; however, Smith & Zientek (1979) proposed that rapid growth with slow diffusion was responsible for other examples of complex zoning in NVF eclogite xenoliths, and it has been invoked for patchy zoning in Cr from orogenic garnet (Fig. 7c; e.g. Yang & Rivers, 2001; Angiboust *et al.*, 2014). What the growth of these patchwork zones and the initial formation of the atoll can tell us about the fluid history of this sample is unclear, but these textural features clearly set it apart from the others in this study.

Pre-emplacment residence time

One of the controversies around the extent of Farallon-age mobilization and recrystallization of these eclogite xenoliths stems from their Proterozoic zircon ages (Smith *et al.*, 2004; Usui *et al.*, 2006; Malik *et al.*, 2017). Sharp prograde major element zone boundaries in garnet have been interpreted as evidence of Farallon-age subduction zone transport, as diffusive resetting would have erased any zoning formed during Proterozoic accretion (e.g. Smith & Zientek, 1979; Helmstaedt & Schulze, 1988; Smith, 2020). We used modeling of $<20\mu\text{m}$ diffusion profiles at zone boundaries and healed fractures in garnets from the 12-97 samples to place quantitative constraints on the timing of garnet fracture healing and rim growth relative to diatreme emplacement.

For garnet rims that record evidence of fluid infiltration, best-fit models for the peak temperature and pressure (620 °C at 3.7 GPa; Hernández-Urbe & Palin, 2019) of the eclogite xenoliths produce durations of 32–190 kyr between fluid infiltration and diatreme emplacement (Figs 8 and 10; Table 3). If the minimum and maximum uncertainty bounds of the temperature estimate are considered ($\pm 50^\circ\text{C}$; Hernández-Urbe & Palin), durations for these low- $\delta^{18}\text{O}$ rims expand to 5 kyr to 5 Myr (Table 3). This strongly suggests a temporal link between low- $\delta^{18}\text{O}$ garnet growth driven by serpentinite-derived fluid infiltration and diatreme emplacement. These short timescales are also comparable with the ~ 3 Myr spread in monazite ages found by Schulze *et al.* (2015) and proposed as the duration of the ‘Great Hydration’ fluid influx (Fig. 10). Results from healed fractures in sample 12-97-45 are similar in duration to low- $\delta^{18}\text{O}$ garnet rims (48–130 kyr; Table 3); however, the healed fracture from 12-97-11 preserves a longer

duration (480 kyr; Table 3). This suggests that healed fractures in some garnets are temporally associated with formation of low- $\delta^{18}\text{O}$ garnet and the ‘Great Hydration’, whereas others may have formed during subduction (e.g. Broadwell *et al.*, 2019). The garnet 12-97-53-A rim zone also preserves a longer duration of 320 kyr (and up to 13 Myr) between rim growth and diatreme emplacement. This longer duration is consistent with the absence of low- $\delta^{18}\text{O}$ garnet rims and supports the idea that any ‘Great Hydration’-related garnet was resorbed (Table 3; Figs 6 and 10). Diffusion modeling results from low- $\delta^{18}\text{O}$ garnet rims establish a temporal link between fluid influx and diatreme emplacement and support models of a ‘Great Hydration’. These temporal relationships suggest that fluid infiltration was not related to steady-state subduction, but instead was the result of processes occurring immediately prior to diatreme emplacement such as slab removal, massive dehydration of the foundering serpentinitized slab mantle, and asthenospheric return flow (Fig. 10).

The presence of inherited garnet from Proterozoic accretion can be assessed from the maximum residence times produced by our models. Maximum residence times of 290 kyr to 13 Myr were generated by our model using the lower bound of the uncertainty in peak temperature (570 °C; Hernández-Urbe & Palin, 2019), with all but sample 12-97-53, which records no isotopic evidence of fluid infiltration, yielding residence times <7.6 Myr (Fig. 10; Table 3). Our longest residence time is two orders of magnitude shorter, and the longest associated with low- $\delta^{18}\text{O}$ values is three orders of magnitude shorter, than the U–Pb zircon ages of the Proterozoic protolith (Smith *et al.*, 2004; Malik *et al.*, 2017). Because of the exponential dependence of diffusivity on temperature, our models robustly constrain the pre-emplacment residence times of the eclogites within the subduction zone. Cold storage at the base of the crust prior to Farallon subduction cannot realistically extend these durations, as storage conditions would have been significantly hotter prior to subduction. Thus, the modeled residence times, particularly those associated with low- $\delta^{18}\text{O}$ garnet, rule out the possibility that any of the zoning preserved in our garnets was inherited from the Proterozoic and requires Farallon-age mobilization and fluid infiltration as has been previously concluded (Smith, 2020).

Bias owing to assumed initial profiles, off-center garnet sections and artificial profile smoothing owing to analytical conditions (convolution effects) is in the direction of longer residence times, making our estimates robust maxima. If the initial concentration profiles in our models were gradual instead of step functions less diffusion would be necessary to reach the measured profiles and our model would yield shorter residence time. Similarly, off-center garnet sections would produce artificially gradual profiles and our model would overestimate residence times. Convolution effects describe the overlapping activation volumes of closely spaced electron microprobe analyses and will act to

Table 3: Results of multi-component garnet diffusion model

Sample	Garnet	Traverse	Duration (years)		
			670 °C	620 °C	570 °C
12-97-11	B	fracture	9.5×10^4	4.8×10^5	7.6×10^6
	B	rim	4.8×10^3	3.2×10^4	2.9×10^5
12-97-45	A	fracture	2.9×10^4	1.3×10^5	1.9×10^6
	A	rim	1.9×10^4	1.9×10^5	1.3×10^6
	A	rim	9.5×10^4	1.9×10^5	4.8×10^6
12-97-53	B	fracture	5.1×10^3	4.8×10^4	5.1×10^5
	A	rim	9.5×10^4	3.2×10^5	1.3×10^7

artificially smooth measured profiles lengthening modeled residence times (e.g. Ganguly *et al.*, 1988). With the given inputs, the upper bound of our ranges can be considered to be a definitive maximum (Table 3).

Implications for a ‘Great Hydration’ and Colorado Plateau uplift

The eclogite xenoliths analyzed in this study point towards a complex fluid history beneath the Colorado Plateau recorded in intra-crystalline $\delta^{18}\text{O}$ and cation zoning in garnet. Here we will synthesize these findings with almost five decades of research on NVF xenoliths to present a model of the lithospheric evolution over the final 10 Myr before diatreme emplacement.

Garnet rims with low- $\delta^{18}\text{O}$ values in this study record infiltration of a serpentinite-derived fluid sourced from the lithospheric mantle of the Farallon slab. Shifts in $\delta^{18}\text{O}$ away from pristine mantle values in peridotite xenoliths also resulted from interaction with a low- $\delta^{18}\text{O}$ slab serpentinite-derived fluid (Marshall *et al.*, 2017). All isotopically zoned garnets in this study converge to the same lower $\delta^{18}\text{O}$ value, a value comparable with that for peridotite xenoliths, suggesting that a single fluid source, possibly a single period of fluid influx, is recorded in all these xenoliths (Fig. 9). In addition to the locally pervasive distribution of this fluid influx preserved in Moses Rock xenoliths, this low- $\delta^{18}\text{O}$ signature is present in xenoliths from Green Knobs diatreme over 100 km away (Marshall *et al.*, 2017). Together with the dominance of SUM in all NVF diatremes, this common low- $\delta^{18}\text{O}$ isotopic signature suggests that the spatial distribution of this fluid influx was of a comparable scale to the NVF, and potentially the Colorado Plateau or greater (e.g. Facer *et al.*, 2009). The stable isotope constraints from eclogite in this study and peridotite xenoliths from previous investigations suggest that a large-scale serpentinite-derived fluid influx hydrated significant portions of the mantle beneath the Colorado Plateau.

Diffusion modeling of low- $\delta^{18}\text{O}$ garnet zones suggests that the timing of fluid influx was probably within 200 kyr (and firmly within 5 Myr) of diatreme emplacement across all eclogite xenoliths. This limited range in residence time for low- $\delta^{18}\text{O}$ garnet zones suggests that this fluid infiltration can be considered as a single, roughly contemporaneous ‘Great Hydration’ event (Fig. 10; Table 3). Schulze *et al.* (2015) first proposed

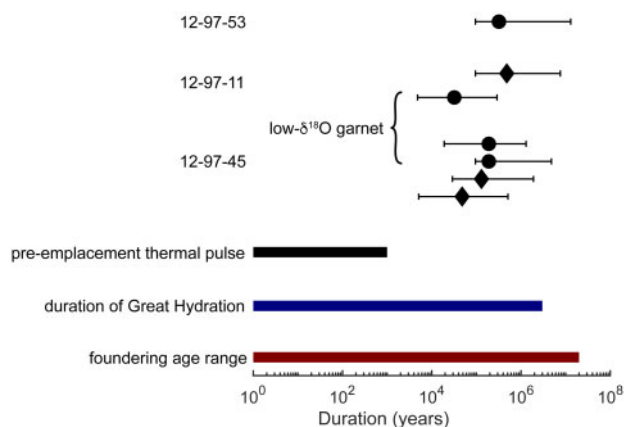


Fig. 10. Diffusion model results from all samples, including those recording the timing of low- $\delta^{18}\text{O}$ fluid infiltration. Best-fit durations from rim zone boundaries are plotted as circles and healed fractures are plotted as diamonds. Error bars show model results incorporating uncertainty in the peak temperature estimate ($\pm 50^\circ\text{C}$; Hernández-Urbe & Palin, 2019). Short timescales between fluid infiltration and diatreme emplacement recorded by low- $\delta^{18}\text{O}$ garnet rims are in agreement with geochronological evidence of a ‘Great Hydration’. The lack of isotopic evidence for fluid infiltration in the rim of garnet 12-97-53-A suggests that it does not preserve evidence of the Great Hydration consistent with the longer durations from diffusion modeling. Maximum duration of a late thermal pulse calculated from Fe–Mg diffusion in olivine in a dunite xenolith is marked by the black bar (Smith, 2010). Two standard deviation range of monazite Th–Pb ages dating the ‘Great Hydration’ is plotted in the blue bar ($n=55$; Schulze *et al.*, 2015). Inferred timing for foundering of the Farallon slab beneath the Colorado Plateau is plotted as the red bar (Coney & Reynolds, 1977; Humphreys, 1995, 2009; Humphreys *et al.*, 2003; Cather *et al.*, 2008; Levander *et al.*, 2011). Timescales derived from diffusion modeling are comparable with the duration of the Great Hydration and foundering of the Farallon plate, suggesting a link between the fluid infiltration recorded in garnet rims and monazite growth and the foundering-induced serpentinite dehydration.

this single ‘Great Hydration’ based on metasomatic monazite ages in Moses Rock eclogite xenoliths with a spread of 3 Myr. They also observed that the ages of ~ 28 Ma overlapped with estimates of diatreme emplacement and minette eruption that ranged from 21 to 30 Ma (e.g. Naeser, 1971; Helmstaedt & Doig, 1975; Roden *et al.*, 1979; Laughlin *et al.*, 1986; Nowell, 1993; Smith *et al.*, 2004). A similar age population between ~ 20 and 35 Ma is also found in U–Pb zircon and Sm–Nd garnet geochronology across NVF eclogite xenoliths and requires fluid to catalyze recrystallization (Wendlandt *et al.*, 1996; Usui *et al.*, 2003; Smith *et al.*, 2004). The overlap between ages of diatreme emplacement and fluid presence in eclogites supports our diffusion modeling results indicating that fluid influx occurred as a single ‘Great Hydration’ and was temporally related to diatreme emplacement.

Diffusion chronometry of subduction-derived peridotite xenoliths constrains the processes occurring in the diatreme source region between the influx of serpentinite-derived fluid and diatreme emplacement (Smith, 2010). Forsterite-rich olivine grown during

chlorite breakdown in response to a thermal pulse ($>800^{\circ}\text{C}$) yields residence times of <1700 years prior to emplacement (Smith, 2010). This thermal pulse is interpreted to be the result of minette magma intrusion into the diatreme source region and could have produced the volatiles thought to drive diatreme emplacement as gas–solid mixtures (e.g. McGetchin & Silver, 1970; Smith, 2010).

The direct connection between fluid influx and diatreme emplacement based on data from eclogite xenolith garnets presented here, and supporting evidence from similar eclogite and peridotite xenoliths across the NVF, allows us to formulate a chronology of events immediately prior to, and up to, diatreme emplacement. At $\sim 28 \pm 1.5$ Ma and within <200 kyr of diatreme emplacement, massive quantities of serpentinite-derived fluids from the mantle lithosphere of the Farallon plate infiltrated the NVF diatreme source region. This fluid influx grew garnet rims and monazite in underplated eclogites, and antigorite and chlorite in mantle peridotites, and recrystallized mantle olivine. Within 200 kyr (and <1700 years prior to diatreme emplacement), minette magma intruded the source region, destabilizing lawsonite and garnet in the eclogites, and dehydrating chlorite and antigorite to form forsterite-rich olivine rims in mantle peridotites. The volatiles given off by chlorite and antigorite dehydration created an unstable volatile and serpentinite mixture that then erupted as SUM within 1700 years.

The best mechanism to produce the temporal, spatial and geochemical characteristics of the ‘Great Hydration’ fluid influx and subsequent thermal pulse and diatreme emplacement is through foundering of the Farallon slab. Inferred timing of slab foundering from 40 to 20 Ma overlaps with monazite, garnet and zircon ages from eclogite xenoliths, emplacement ages of the diatremes, and with the timing of fluid influx and a late thermal pulse from diffusion modeling, favoring a role for foundering in these processes (e.g. Naeser, 1971; Coney & Reynolds, 1977; Roden *et al.*, 1979; Humphreys, 1995; Wendlandt *et al.*, 1996; Usui *et al.*, 2003; Cather *et al.*, 2008; Smith, 2010; Schulze *et al.*, 2015). Subvertical sinking of the Farallon slab into the asthenosphere would have led to widespread slab heating, dehydrating the remaining serpentinite nearly simultaneously over a large area. Slab foundering would have also been followed by asthenospheric return flow that could have driven minette intrusion and dehydration within the recently hydrated mantle necessary for diatreme emplacement.

The evidence across four eclogite xenoliths for a single common fluid influx strongly supports the role of a ‘Great Hydration’ in Colorado Plateau uplift. A single fluid release of this scale could add significantly to the estimated 13% serpentinitization necessary to uplift the plateau to its current position (Schulze *et al.*, 2015). Further study of the NVF eclogite xenoliths as well as other lithologies could shed more light on the spatial and temporal distribution of the ‘Great Hydration’ as

well as its relationship to slab detachment and minette intrusion. The discovery of oxygen isotope zoning in these xenoliths opens the possibility for a more detailed record of fluid interaction and mantle metasomatism beneath the Colorado Plateau, and, although the NVF xenoliths are unusual, the re-evaluation of assumed isotopic homogeneity in some mantle xenoliths may be warranted.

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SUPPLEMENTARY DATA

Supplementary data are available at *Journal of Petrology* online.

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