

Water contents of Roberts Victor xenolithic eclogites: primary and metasomatic controls

Jin-Xiang Huang · Pei Li · William L. Griffin ·
Qun-Ke Xia · Yoann Gréau · Norman J. Pearson ·
Suzanne Y. O'Reilly

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Abstract A suite of eclogites from the Roberts Victor kimberlite has been extensively characterized in terms of petrology and geochemical compositions (Gréau et al. in *Geochim Cosmochim Acta* 75(22):6927–6954, 2011; Huang et al. in *Lithos* 142–143:161–181, 2012a). In the present study, the water contents of eclogitic garnet and omphacite were analyzed by Fourier transform infrared spectrometry. Garnet does not contain measureable OH in any sample. The water content of omphacite in the studied eclogites ranges from 211 to 1,496 ppm. Mantle metasomatism has modified the water content of some of the eclogites, while others retain water contents characteristic of their original environment. The OH contents of the metasomatized eclogites may be mainly controlled by the H₂O fugacity and mineral compositions. The OH contents of the non-metasomatized samples are interpreted to be more sensitive to their mantle equilibration temperature, pressure, and the local fugacities of H₂O and O₂. The calculated

water content of the metasomatic medium is similar to that of carbonatitic–kimberlitic melts/fluids. Eclogites contain more water than peridotites recorded in the literature (341 ± 161 vs 122 ± 54 ppm) and represent an important water reservoir in the lithospheric mantle wherever they occur. This is an important parameter to be considered in the interpretation of mantle processes and geophysical data such as seismic wave speeds and electrical conductivity, and in geodynamic modeling.

Keywords Eclogites · Xenoliths · Water content · Mantle metasomatism · Kaapvaal craton

Introduction

Hydrogen (H), as one of the main volatile elements, plays an important role in Earth's evolution and dynamics (Dasgupta and Dixon 2009; and references therein). It is incorporated into many Earth materials; it is a major constituent in low-pressure hydrous compounds (e.g., gypsum, goethite) and some rock-forming minerals (e.g., mica and amphibole); it also occurs in nominally anhydrous minerals (NAMs), such as feldspar and quartz in the Earth's crust and olivine, orthopyroxene (opx), clinopyroxene (cpx), and garnet (gnt) in the mantle. In NAMs, hydrogen is usually incorporated as point defects and bound to oxygen anions on the edge of the coordination polyhedron; it occurs as hydroxyl and can be considered as a proxy for water content. Although NAMs contain trace amounts of hydrogen, equivalent to less than several hundred ppm of H₂O (Keppler and Smyth 2006), the mantle is a potentially large reservoir for water because of its huge volume, consisting mainly of such NAMs (Beran 1999; Ohtani 2005). The presence of water in the mantle affects many of Earth's

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J.-X. Huang (✉)
State Key Laboratory of Lithospheric Evolution, Institute
of Geology and Geophysics, China Academy of Sciences,
P.O. Box 9825, Beijing 100029, China
e-mail: jinxiang.huang@mq.edu.au

J.-X. Huang · W. L. Griffin · Y. Gréau · N. J. Pearson ·
S. Y. O'Reilly
Australian Research Council Centre of Excellence for Core
to Crust Fluid Systems (CCFS) and GEMOC, Department
of Earth and Planetary Sciences, Macquarie University,
North Ryde, NSW 2109, Australia

P. Li · Q.-K. Xia
CAS Key Laboratory of Crust-Mantle Materials
and Environments, School of Earth and Space Sciences,
University of Science and Technology of China, Hefei, China

properties (e.g., rheology, electrical and thermal conductivity, and seismic wave velocities) and geological processes (e.g., rock melting, mineral deformation, and element diffusion) (Hirth et al. 2000; Mei and Kohlstedt 2000a, b; Hofmeister 2004; Hier-Majumder, et al. 2005; Médard and Grove 2008; Zheng et al. 2011; Demouchy et al. 2012).

The water content of the mantle has been estimated previously, based on analysis of NAMs in peridotites derived from both continental and oceanic lithospheric mantle (e.g., Peslier et al. 2002; Matsyuk and Langer 2004; Li et al. 2008; Yang et al. 2008; Peslier 2010; Xia et al. 2010; Yu et al. 2011; Peslier et al. 2012) and basaltic glasses (Pineau and Javoy 1994; Ligi et al. 2005; Workman et al. 2006). However, eclogites, a minor but important component of the mantle (Huang et al. 2012a), have not previously been well characterized for their water content (Aines and Rossman 1984; Smyth et al. 1991; Bell and Rossman 1992; Koch-Muller et al. 2004; Katayama et al. 2006).

In the cratonic mantle, eclogites are commonly concentrated in a layer ~20 km thick around the lithosphere-asthenosphere boundary, as estimated from chemical sections constructed from xenoliths and xenocrysts from kimberlite pipes (Griffin and O'Reilly 2007). Their origins can be attributed to two end-member processes; either subducted oceanic crust (Barth et al. 2001; Jacob 2004; Aulbach et al. 2007; Smart et al. 2012) or crystallization of magmas derived from the deeper Earth (Hatton and Gurney 1987; Griffin and O'Reilly 2007). Greater complexity is introduced by several studies showing that most samples have been heavily modified by metasomatic processes (Gréau et al. 2011; Huang et al. 2012a; Gréau et al. 2013). If they represent metamorphosed oceanic basalts/gabbros, their water contents would provide critical information on water recycling into the mantle. If they represent direct magmatic products crystallized in the deep mantle, their water contents may elucidate the behavior of OH in Earth's interior. Regardless of which model for eclogite formation is relevant for the eclogites in particular localities, their water contents can provide additional information on how water is distributed in mantle phases and how much water the mantle might store.

The suite of xenolithic eclogites from the Roberts Victor kimberlite in South Africa has been well studied previously, and they have been classified into Types I and II in terms of mineral compositions and microstructures. In Type I eclogites, garnets contain ≥ 0.07 wt% Na_2O and cpx ≥ 0.08 wt% K_2O , while in Type II gnt and cpx have lower contents of these elements (MacGregor and Carter 1970; McCandless and Gurney 1986; Schulze et al. 2000; Gréau et al. 2011; Huang et al. 2012a, b). Furthermore, Gréau et al. (2011) and Huang et al. (2012a) showed that the volumetrically dominant Type I eclogites formed through extensive metasomatism of Type II eclogites by carbonatitic–kimberlitic

melts/fluids. In this study, we present the water contents of those eclogites, to examine systematically the differences between Type I and II eclogites, to estimate the water content of the metasomatic melts/fluids, and to further constrain the origins of Type II eclogites.

Samples

The samples studied in this paper are bimineralic eclogites from the Roberts Victor kimberlite pipe, South Africa. Roberts Victor is located inside the Kaapvaal craton and its kimberlites (Group II) erupted at 128 ± 15 Ma (Smith, et al. 1985). The samples include both Type I and II eclogites. Type I eclogites are further subdivided into Type IA (gnt FeO > 17 %) and IB (gnt FeO \leq 17 %); Type II eclogites have two subgroups, Type IIA (gnt MgO > 12 %) and IIB (gnt MgO \leq 12 %) as defined by Huang et al. (2012a). Type I eclogites have subhedral to rounded garnets in a matrix of altered cpx; Type IB eclogites are generally more altered than Type IA. Both Type IIA and IIB eclogites studied here are fresh. Their gnt and cpx show an interlocking microstructure, and the gnt grains commonly define a lineation. These eclogites have homogeneous mineral compositions. Their equilibrium temperatures (T) at any pressure (P) can therefore be estimated using the Mg–Fe exchange thermometer (Krogh 1988); the corresponding P and thus depth are estimated from the intersection of the P–T line derived from the thermometry calculations with the local geotherm derived from garnet xenocrysts and garnet peridotite xenoliths (Griffin and O'Reilly 2007; Huang, et al. 2012a). Type IA and IB eclogites give similar temperatures/depths at ~1,100 °C/~180 km and 1,135 °C/~185 km, respectively. Type IIA eclogites have much lower temperatures (895–1,063 °C) than Type IIB (1,183–1,300 °C), corresponding to 168–180 and 189–198 km. Detailed petrographic descriptions, chemical compositions, and geothermobarometry conditions are given by Gréau et al. (2011), Huang et al. (2012a) and in “Appendix”.

Analytical methods

Doubly polished sections with a thickness 0.15–0.2 mm were prepared for analysis by Fourier transform infrared spectroscopy (FTIR). The sections were dried in an oven at 110 °C for ~6 h after being cleaned in ethanol, before the measurements. A Nicolet 5700 FTIR spectrometer coupled with a Continuum microscope at the University of Science and Technology of China was used to collect the unpolarized spectra from 1,000 to 5,000 cm^{-1} . A total of 128 scans were accumulated for each spectrum at a 4 cm^{-1} resolution.

The aperture size was generally around $50 \times 50 \mu\text{m}$. Areas free of inclusions and cracks were chosen for the analyses.

As infrared spectra are not rigorously self-calibrating, further calculations are needed to give the final OH contents of the analyzed minerals. A modified equation of the Beer-Lambert law was used to calculate the OH content of the omphacite:

$$c = \Delta / (I \times t \times \Upsilon)$$

where c is the content of hydrogen species (ppm H_2O by wt), Δ is the integrated area (cm^{-2}) of absorption bands in the region of interest, I is the integral specific absorption coefficient ($\text{ppm}^{-1} \text{cm}^{-2}$), t is thickness, and $\Upsilon = 1/3$ (Gibson et al. 2013). OH absorption bands were integrated between $3,000$ and $3,800 \text{cm}^{-1}$ to obtain Δ data. The baseline corrections were carried out by hand at least three times for each spectrum. The equation $I = 8.34 \pm 1.46 \times 10^4$ ($\text{L mol}^{-1} \text{cm}^{-2}$), derived from the OH study of omphacite in eclogites from the Kokchetav massif by both FTIR and SIMS (Katayama et al. 2006), is used in this study. The most commonly used integral absorption coefficient for mantle cpx is given by Bell et al. (1995). However, this coefficient is only accurate for augite, not the entire mineral group. The direct use of the augite coefficient for omphacite is not adequate because omphacite and augite give quite different spectra. The $3,445\text{--}3,470 \text{cm}^{-1}$ band in omphacite spectra is normally much stronger than the other two while the $\sim 3,620 \text{cm}^{-1}$ band is usually the most intense one in augite spectra (Paterson 1982; Skogby et al. 1990; Bell et al. 1995; Skogby 2006). The absolute intensity of absorption, which determines the absorption coefficient of specific minerals, is frequency dependent. That is, it is a function of hydrogen bond length in an $\text{O}\text{--}\text{H}\cdots\text{O}$ hydrogen-bonded system, and the intensity of the OH band

is usually higher when the band occurs at a lower wave number (Paterson 1982; Libowitzky and Beran 2006; Balan et al. 2008). The uncertainties arising from the use of unpolarized infrared beams on unoriented minerals, the baseline correction, and the sample thickness are estimated to be 20–30 % (Xia et al. 2010).

Results

At least 6 grains of garnet (gnt) in each sample were measured; none of them had detectable bands in the $3,000\text{--}4,000 \text{cm}^{-1}$ range, showing that they are anhydrous within the precision of this method.

All cpx grains in the xenolithic eclogites are omphacite, and they show three hydroxyl absorption bands in IR unpolarized spectra; $3,445\text{--}3,470$, $3,510\text{--}3,540$, and $3,610\text{--}3,630 \text{cm}^{-1}$. The $3,445\text{--}3,470 \text{cm}^{-1}$ band is generally much stronger than the other two (Fig. 1). Cpx grains in Type IA, IB, IIA, and IIB eclogites give similar spectra with different relative band intensities (Fig. 1). Six out of 473 analyzed grains in this study show a strong $3,610\text{--}3,630 \text{cm}^{-1}$ band and a band at $3,250 \text{cm}^{-1}$; their $3,445\text{--}3,470 \text{cm}^{-1}$ band is at higher wave number than those of other grains (Fig. 1). This unusual spectrum is not included in the final calculation of water contents as the analyzed spot might be contaminated with other materials. The crystal orientation with respect to the infrared beam direction may vary from grain to grain; therefore, different grains of the same sample give variable relative absorbance of the hydroxyl bands. To minimize the uncertainties arising from this variability, about 20 grains in each sample were analyzed where possible and the averaged result was used.

Fig. 1 Representative unpolarized IR spectra of omphacite grains from Type IA, IB, IIA, and IIB Roberts Victor xenolithic eclogites

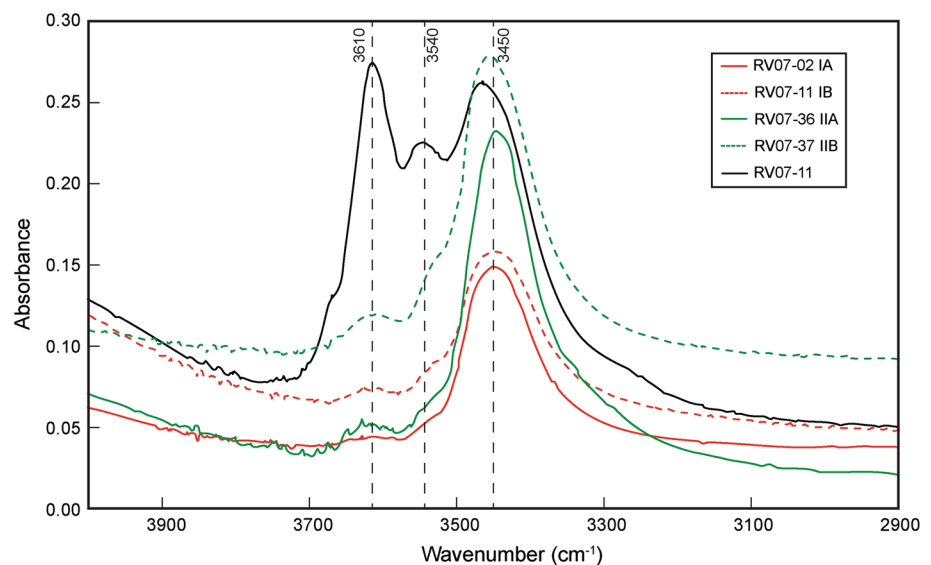


Table 1 Water content of omphacite in Roberts Victor eclogites and related information

Sample No.	Type	Grain No.	H ₂ O (ppm) in cpx	30 % error	Density (g cm ⁻³)	Density (g cm ⁻³)	H ₂ O (ppm) whole rock	Temp. (°C)	Depth (km)	Calculated H ₂ O (wt%) for mantle melt/fluid equilibrated with eclogites
					Gnt	Cpx				
RV07-02	IA	18	554	166	3.78	3.37	261	1,122	185	4.5
RV07-03	IA	18	315	95	3.79	3.39	149	1,227	193	2.9
RV07-13	IA	20	791	237	3.79	3.38	373	1,109	184	6.1
RV07-20	IA	16	341	102	3.78	3.39	161	1,120	184	3.3
RVF-5	IA	12	211	63	3.78	3.37	99	1,112	184	1.6
RVF-7	IA	20	1,337	401	3.79	3.39	631	1,125	185	10.3
RVF-8	IA	19	815	245	3.78	3.37	384	1,108	184	5.8
RV07-01	IB	20	416	125	3.77	3.36	196	1,117	184	3.6
RV07-07	IB	17	637	191	3.77	3.37	300	1,129	185	5.0
RV07-11	IB	18	852	256	3.77	3.37	402	1,114	184	7.3
RV07-14	IB	19	602	180	3.77	3.36	284	1,126	185	4.7
RV07-16	IB	20	586	176	3.75	3.10	265	1,166	188	4.4
RV07-18	IB	18	727	218	3.77	3.34	342	1,133	186	6.1
RV07-19	IB	14	1,001	300	3.76	3.19	460	1,158	187	8.0
HRV?b	IIA	20	342	103	3.78	3.36	161	926	170	2.5
HRV344	IIA	18	361	108	3.77	3.33	169	928	170	3.0
HRV345b	IIA	20	496	149	3.78	3.36	234	911	169	3.5
HRV58-2	IIA	20	639	192	3.79	3.38	301	963	173	5.6
RV07-12	IIA	10	342	103	3.78	3.39	162	988	175	3.1
RV07-36	IIA	17	764	229	3.79	3.39	361	1,063	180	7.0
HRV175-2	IIB	21	914	274	3.77	3.38	432	1,141	186	7.8
HRV316-2	IIB	15	1,496	449	3.74	3.31	702	1,228	193	13.4
RV07-08	IIB	21	911	273	3.76	3.36	430	1,184	189	7.8
RV07-31	IIB	18	1,086	326	3.76	3.38	515	1,209	191	9.3
RV07-33	IIB	15	972	292	3.76	3.39	461	1,279	196	8.1
RV07-34	IIB	19	1,454	436	3.74	3.11	661	1,300	198	11.5
RV07-37	IIB	10	675	203	3.77	3.38	319	1,183	189	5.8

The OH content of omphacite in each eclogite sample is given in Table 1. Type IA samples generally contain somewhat less H₂O than Type IB: 211–1337 (median 554) ppm in Type IA and 416–1001 (median 637) ppm in Type IB. The H₂O contents of Type IIA and IIB samples vary from 342 to 764 (median 429) ppm and from 675 to 1,496 (median 972) ppm, respectively.

Discussion

Data evaluation

None of the garnets in this study contains detectable OH. Since H in gnt is not considered to be lost during the ascent of the sample in the kimberlite (Peslier 2010), these

observations suggest that H is not compatible in the garnet crystal structure under high pressure. An experimental study (Withers et al. 1998) suggested that garnet becomes more hydrous with pressure only up to 5 GPa, and that the OH content decreases rapidly with further increase in P, falling below the detection limit even under H₂O-saturated conditions. The estimated depths for the Roberts Victor eclogites are 170–200 km (5.4–6.4 GPa; Huang et al. 2012a), and the anhydrous nature of their garnets is thus consistent with available experimental data.

Submicroscopic amphibole lamellae may occur in the pyroxene structure because of alteration (e.g., Griffin and Murthy 1968; Buseck et al. 1980; Ingrin et al. 1989); such lamellae give an OH band at ~3,675 cm⁻¹ in the FTIR spectra (Skogby et al. 1990). However, this band was not found in any of the spectra in this study, indicating that

amphibole does not contribute to the calculated OH content of these omphacites.

Sheet silicates such as clinocllore and amesite have been reported in the omphacite of Yakutian eclogites. It has been suggested that these phases cause the 3,610–3,630 cm^{-1} band in the omphacite spectrum (Koch-Muller et al. 2004). However, this band is normally interpreted to be caused by the intrinsic OH. The absorption bands at high frequency, such as those at 3,590 and 3,690 cm^{-1} in the spectrum of synthesized orthoenstatite, have been suggested to relate to the Si vacancies (Balan et al. 2013). This may be the case for the 3,610–3,630 cm^{-1} band in the omphacite. In general, it is not clear how widespread these sheet silicates are in the omphacite analyzed here, nor what is the true origin of the band 3,610–3,630 cm^{-1} at this stage. However, this does not affect our understanding of the OH content of omphacites in Roberts Victor eclogites as (1) the intensity of the 3,610–3,630 cm^{-1} band is generally low in the omphacite spectra and accounts for only 10–20 % of the total OH content; (2) this work is focused on comparisons between the water contents of different types of eclogites and their relationships, which vary well outside this potential uncertainty.

Implications of the data

Has H of the omphacite in the xenolithic eclogites been disturbed during the ascent of the xenolith from depth? Can the OH values reflect the water content of the rocks in the upper mantle?

Hydrogen diffuses rapidly in pyroxenes at magmatic temperatures (Ingrin et al. 1995; Hercule and Ingrin 1999; Woods et al. 2000; Stalder and Behrens 2006; Sundvall et al. 2009). It would not be surprising whether H either diffuses out or is incorporated into the mineral structure even during the rapid ascent of the xenolith from the deep Earth (Ingrin and Skogby 2000). However, it is widely accepted that in general, mantle pyroxenes can preserve their water contents from their source regions, because the sample chemistry, the equilibrium conditions, and the OH contents show systematic correlations (Peslier et al. 2002; Bell et al. 2004; Katayama et al. 2006). Furthermore, there is no recognized zonation of OH content recorded in pyroxenes from xenoliths (Grant et al. 2007; Peslier 2010; Sundvall and Stalder 2011), indicating that there is no significant loss or gain of H in pyroxenes, at least during their transport in host magma. The samples analyzed in this paper show homogeneous OH contents across each grain. The samples, Type I in particular, also show general correlations between the contents of OH and trace elements (e.g., Sr and Nd) that are thought to be unaffected by the host magma when the xenoliths are brought up to the surface rapidly (Wilson and Head III 2007; O'Reilly and Griffin 2010). The water

contents of Type II eclogites show broad correlations with concentrations of major elements (e.g., $\text{Ca}^{2+} + \text{Na}^+$, ${}^{\text{IV}}\text{Al}^{3+}$, and Fe^{3+}), which do not change during the transport, but Type I (metasomatized samples) do not (Fig. 2; Table 2), indicating that the samples may preserve information on water content in their source before the kimberlite eruption.

Therefore, the measured OH contents of Roberts Victor eclogites from this study will be regarded as reflecting their water content during their residence in the mantle.

Controls on water content

Where does hydrogen reside and what controls its content in NAMs such as omphacite?

Hydrogen does not occupy a normal cation site in a mineral. H enters the lattice as proton attached to structural oxygen, that is, original O^{2-} is replaced by OH^- (Rossman 1996). The resulting charge excess is balanced by cation vacancies in the structure or by a charge-deficient substitution such as the exchange of Al for Si (Skogby et al. 1990; Skogby 1994). Its compatibility and content are not systematic, but strongly depend on both internal and external factors.

The internal factors are crystal chemistry and lattice structure. In the general formula of pyroxene $(\text{M2})(\text{M1})(\text{Si,Al})_2\text{O}_6$, the M1 and M2 sites incorporate the main cations except Si^{4+} . The M2 site is largely occupied by Ca^{2+} and Na^+ in omphacite and the M1 position by other elements. X-ray crystal structure refinements and analytical TEM analyses of omphacite from xenolithic eclogites show that vacancies, which can balance the charge after H incorporation, are largely constrained to the M2 site (McCormick 1986). The intensity of the band near 3,460 cm^{-1} , the strongest peak band in the omphacite spectrum, is related to the abundance of M2 cation vacancies (Smyth et al. 1991; Koch-Muller et al. 2004). Experimental work on synthetic water-saturated jadeite and Na-rich cpx also suggests that vacancies on the M2 site are very important for H incorporation (Bromiley and Keppeler 2004). Computer modeling using molecular mechanics simulation techniques also indicates that the vacancies should favor the M2 site (Gatzemeier and Wright 2006). The position of the main band of the omphacite spectrum at $\sim 3,460 \text{ cm}^{-1}$ further indicates that the OH dipole direction is oriented roughly parallel to the Υ index of refraction, which can be achieved by the existence of M2 vacancies (Libowitzky and Beran 2006). Therefore, the levels of vacancies in the M2 site would largely constrain the OH content of the omphacite. The OH contents of omphacite in the Type IA, IB, and IIA eclogites show a broad negative correlation with $\text{Ca} + \text{Na}$ contents, respectively (Fig. 2a); higher $\text{Ca} + \text{Na}$ contents allow fewer vacancies in the M2 site, thus restricting entry of H into the omphacite structure; this further supports the relationship

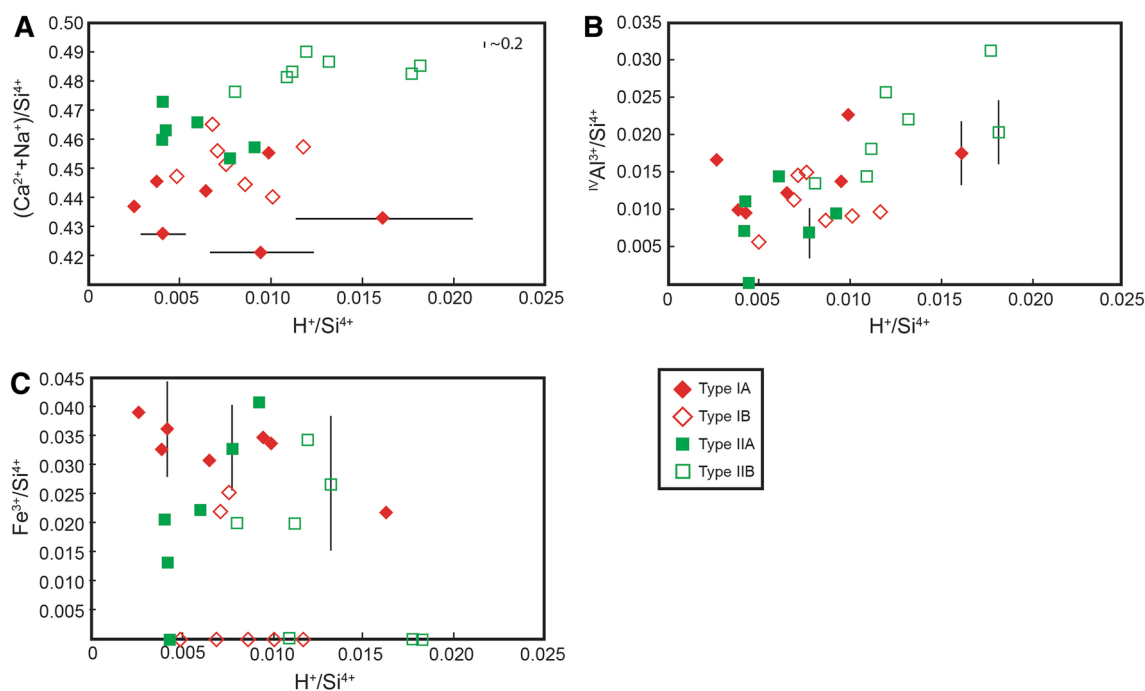


Fig. 2 Plot of calculated $(\text{Ca}^{2+}+\text{Na}^+)/\text{Si}^{4+}$ (a), ${}^{\text{IV}}\text{Al}^{3+}/\text{Si}^{4+}$ (b), and $\text{Fe}^{3+}/\text{Si}^{4+}$ (c) values and $\text{H}^+/\text{Si}^{4+}$ in omphacite for Roberts Victor xenolithic eclogites. Cations are calculated from the electron probe and FTIR data, based on six oxygens in the pyroxene formula unit. The errors are estimated from the standard deviation of the average

values for each sample and include the error propagation during the calculation of the structural formula. The error bars for representative samples are shown in figures; the individual values can be found in Table 2. Original major-element data are from Gréau et al. (2011) and Huang et al. (2012a)

between M2-site vacancies and the OH content of omphacite. However, a positive correlation is seen in Type IIB samples, indicating that the OH content of omphacite in Type IIB eclogites might be controlled by other factors.

Aluminum in the tetrahedral position of omphacite seems to be correlated with the absorbance of bands in the $3,500\text{--}3,530\text{ cm}^{-1}$ region, which gave a positive correlation with the absorption coefficients for this band in studies of Yakutian eclogitic omphacites (Koch-Muller et al. 2004). Experimental studies also show that incorporation of hydrogen into the pyroxene is closely related to the Al content of the tetrahedral site (Tenner et al. 2009; O'Leary et al. 2010). However, the number of ${}^{\text{IV}}\text{Al}^{3+}$ atoms per formula unit in Type I samples does not show any correlation with the water content, while a broad correlation can be seen in Type II samples (Fig. 2b; Table 2). This indicates that little of the OH in Type I samples is related to ${}^{\text{IV}}\text{Al}^{3+}$; but its distribution in Type II may depend on ${}^{\text{IV}}\text{Al}^{3+}$.

The external conditions influencing the OH content of samples include the equilibration T and P, and the local fugacities of H_2O , H_2 , and O_2 . Thermodynamic calculations indicate that clinopyroxenes from samples that equilibrated at high T in the eclogite stability field will contain more vacancies in the structure (Gasparik 1986),

and hence can accommodate more water than lower-T samples. Roberts Victor Type II eclogites show a positive correlation between OH contents and equilibration temperatures (Fig. 3a), which is consistent with this inference. Most Type I samples fall within a narrow range of equilibration temperatures at $\sim 1,120\text{ }^\circ\text{C}$; therefore, it is hard to tell whether their water contents are affected by the temperature. Type I eclogites show a wide range of OH contents (Fig. 3), and they have been heavily metasomatized, so their water content may be determined by the H_2O fugacity, as well as the mineral compositions (see discussion above).

Type IIA omphacites show a positive correlation between $\text{H}^+/\text{Si}^{4+}$ and $\text{Fe}^{3+}/\text{Si}^{4+}$, whereas Type IIB give a broad negative correlation; Type IA samples show a negative correlation, and only two Type IB samples contain calculated Fe^{3+} (Fig. 2c; Table 2). This suggests that Type I, IIA, and IIB samples may have equilibrated under different oxygen-fugacity conditions, and that this may have played a role in controlling their water content.

It is not surprising that the OH contents of Roberts Victor eclogites are controlled or affected by different factors, as they have experienced different geological processes. Type I eclogites have been heavily metasomatized by melts/fluids in the carbonatitic–kimberlitic spectrum in the

Table 2 Calculated element ratios of omphacite in Roberts Victor eclogites

Sample No.	Type	H ⁺ /Si ⁴⁺	1SD	(Ca ²⁺ +Na ⁺)/Si ⁴⁺	1SD	^{IV} Al ³⁺ /Si ⁴⁺	1SD	Fe ³⁺ /Si ⁴⁺	1SD
RV07-02	IA	0.0065	0.0019	0.442	0.003	0.012	0.003	0.031	0.012
RV07-03	IA	0.0038	0.0011	0.445	0.011	0.010	0.006	0.033	0.027
RV07-13	IA	0.0095	0.0028	0.421	0.005	0.014	0.005	0.035	0.017
RV07-20	IA	0.0041	0.0012	0.428	0.003	0.010	0.003	0.036	0.010
RVF-5	IA	0.0026	0.0008	0.437	0.016	0.017	0.006	0.039	0.029
RVF-7	IA	0.0162	0.0048	0.433	0.002	0.017	0.004	0.022	0.014
RVF-8	IA	0.0099	0.0029	0.455	0.009	0.023	0.002	0.034	0.016
RV07-01	IB	0.0049	0.0015	0.447	0.004	0.005	0.004	0	0
RV07-07	IB	0.0076	0.0022	0.451	0.005	0.015	0.004	0.025	0.015
RV07-11	IB	0.0101	0.0030	0.440	0.004	0.009	0.004	0	0
RV07-14	IB	0.0071	0.0021	0.456	0.009	0.015	0.002	0.022	0.015
RV07-16	IB	0.0069	0.0020	0.465	0.004	0.011	0.003	0	0
RV07-18	IB	0.0086	0.0026	0.444	0.014	0.008	0.004	0	0
RV07-19	IB	0.0117	0.0035	0.457	0.007	0.010	0.002	0	0
HRV?b	IIA	0.0041	0.0012	0.460	0.010	0.011	0.002	0.013	0.017
HRV344	IIA	0.0043	0.0013	0.462	0.014	0.000	0.005	0	0
HRV345b	IIA	0.0060	0.0018	0.465	0.009	0.015	0.010	0.022	0.037
HRV58-2	IIA	0.0078	0.0023	0.453	0.002	0.007	0.003	0.033	0.008
RV07-12	IIA	0.0041	0.0012	0.473	0.011	0.007	0.004	0.021	0.026
RV07-36	IIA	0.0092	0.0027	0.457	0.006	0.010	0.004	0.041	0.016
HRV175-2	IIB	0.0112	0.0034	0.483	0.006	0.018	0.002	0.020	0.013
HRV316-2	IIB	0.0182	0.0054	0.485	0.006	0.020	0.004	0	0
RV07-08	IIB	0.0109	0.0033	0.481	0.004	0.014	0.002	0	0
RV07-31	IIB	0.0132	0.0040	0.486	0.006	0.022	0.002	0.027	0.014
RV07-33	IIB	0.0120	0.0036	0.490	0.007	0.026	0.003	0.034	0.019
RV07-34	IIB	0.0178	0.0052	0.482	0.000	0.031	0.005	0	0
RV07-37	IIB	0.0081	0.0024	0.476	0.003	0.013	0.004	0.020	0.014

Cations are calculated from the electron probe data based on six oxygens in the formula unit

mantle while Type II eclogites have apparently escaped the influence of these metasomatic fluids (Gréau et al. 2011; Huang et al. 2012a).

Metasomatism versus water content

Studies of xenolithic peridotites from several localities in the Kaapvaal craton have indicated that the water content of this cratonic mantle is strongly controlled by metasomatism (Peslier et al. 2012). Such metasomatism also affected the Roberts Victor eclogites, which are stored in a ~20 km layer around the lithosphere-asthenosphere boundary at the base of the cratonic root (Fig. 3b) (Huang et al. 2012a). We have suggested previously that Type II eclogites were progressively metasomatized by melts/fluids in the carbonatitic to kimberlitic spectrum to form first Type IA and then Type IB eclogites (Huang et al. 2012a, 2014). The water contents of Type IA omphacites cover a wide range (211–1,337 ppm), while Type IB samples are generally less variable, from 416 to 1,001 ppm, with higher median water content than in Type IA (637 vs 554 ppm) (Fig. 3).

The water content of the melts/fluids in equilibrium with Type I eclogites (Table 1) has been calculated using the experimental partition coefficients between cpx and silicate melt at 1.5 GPa and 1,275–1,350 °C given by O'Leary et al. (2010); no other partition coefficient is available for the Type I samples equilibrated at 5.4–6.4 GPa. $D_{\text{H}_2\text{O}}^{\text{Cpx-Melt}}$ is sensitive to pressure; therefore, the calculated results shown here need to be treated with caution.

The calculated melts/fluids equilibrated with Type IA samples have water contents from 1.7 to 10.3 wt% (average 4.0 %, excluding one value at 10.3 %), and those equilibrated with Type IB contain 3.6–8.0 wt% H₂O (average 5.6 %). These estimates overlap the water content of kimberlitic magmas (5–10 wt%; Kavanagh and Sparks 2009; Sokol et al. 2013), consistent with the interpretation that Type IB eclogites were modified by kimberlite-related melts/fluids shortly before eruption (Huang et al. 2012a). Kimberlitic melts are part of a compositional spectrum extending to carbonatites (Gudfinnsson and Presnall 2005; Girniss et al. 2011; Sokol et al. 2013), which may contain less water than kimberlitic melts. It is hard to constrain the

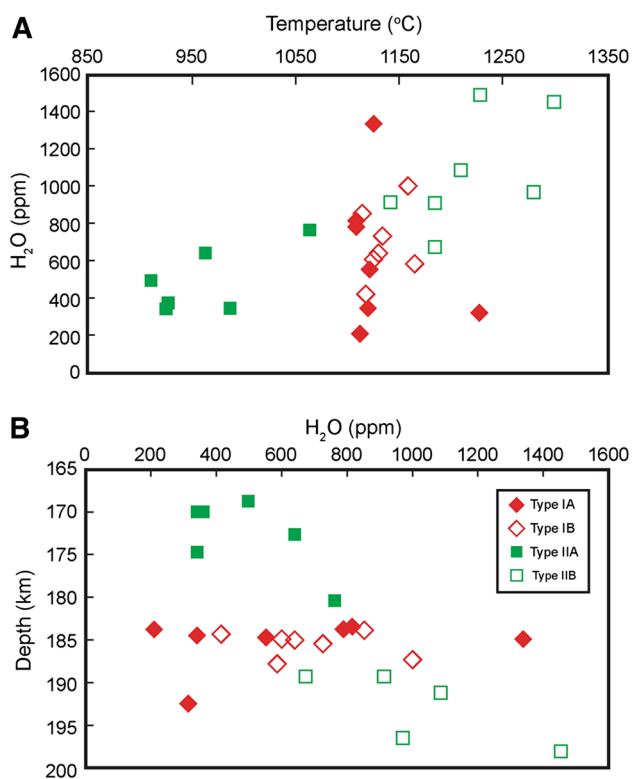


Fig. 3 Plot of calculated mantle equilibration temperatures (a) and depths (b) of eclogite versus H_2O content of omphacite in Roberts Victor xenolithic eclogites

source(s) of the carbonatitic–kimberlitic melts/fluids that metasomatized the Roberts Victor eclogites with available information, although Peslier et al. (2012) argued that the metasomatic agents that affected the Kaapvaal cratonic mantle were mainly derived from subducted materials, based on the similarity of H_2O/Ce ratios between arc-related melt inclusions and the calculated melts in equilibrium with the peridotite xenoliths in kimberlites.

Eclogite origins and water content

Understanding the origin of xenolithic eclogites can help to constrain models of lithospheric mantle formation and improve geodynamic interpretations. Type II eclogites are the least metasomatized samples in the Roberts Victor suite and may preserve some primary compositional information, while the original compositions of Type I eclogites have been completely changed by metasomatism (Gréau et al. 2011; Huang et al. 2012a). Type II eclogites have two subgroups, Type IIA and IIB, which have different major-element compositions but similar trace-element and isotopic compositions; Type IIB are generally more depleted in trace elements than Type IIA (Gréau et al. 2011; Huang et al. 2012a). The relationships between these two subgroups and

their origin(s) are not clear. Spatially, Type IIB eclogites come from the base of the eclogite-rich domain, much closer to the asthenosphere, while Type IIA eclogites occupy the top of this horizon (Figs. 3b, 4). Type IIB eclogites contain much more water than Type IIA; 675–1,496 ppm (median 972) in Type IIB omphacite compared with 342–764 ppm (median 429) in Type IIA. It is not clear to what level the water contents of Type IIA and IIB omphacite are related to the M2 site (Fig. 2a). Their water contents may be affected by $^{IV}Al^{3+}$ to some extent as discussed above (Fig. 2b).

The OH contents of Type IIB omphacite are negatively correlated with Fe^{3+}/Si^{4+} (Fig. 2c), suggesting that Type IIB samples were formed from, and/or affected later by, oxidized melts/fluids. OH^- would have been generated by consuming Fe^{3+} in omphacite and O_2 in the melts/fluids. The more water that was formed, the more Fe^{3+} was consumed, and the lower the Fe^{3+}/Si^{4+} of the omphacite. However, Type IIA omphacites show a positive correlation between OH content and Fe^{3+}/Si^{4+} (Fig. 2c), indicating that an unrecognized factor other than O_2 fugacity may have controlled their water contents.

If no secondary process has affected the Type II eclogites after formation, the measured water content of their omphacites can reflect the primary water content of these samples. As it is not clear whether Type II eclogites are direct products of magma crystallization at depth, or represent the metamorphic equivalent of oceanic gabbros, we discuss these two scenarios separately.

Scenario 1: If Type II eclogites have been generated directly from the magma and have reequilibrated to ambient PT conditions at the base of the lithosphere, and the water content of the omphacite may reflect, if only indirectly, equilibrium with the parental melt. The calculated water content of silicate melts that might have been in equilibrium with Type IIA omphacites is ~4 %; for Type IIB omphacites, the corresponding value is ~9 % (Table 1). Do these melts have different water contents because they reflect different sources, or different stages of evolution? Type IIA omphacite has much lower water contents than Type IIB. Type IIB seems to be affected more by variations in oxidation state than Type IIA. Therefore, Type IIA and IIB are more likely to be the products of two separate magmatic processes or at least of two episodes within one event; they give similar mineral isochron ages (Huang et al. 2012a).

Scenario 2: If Type II eclogites are the metamorphic equivalent of subducted oceanic gabbros, they must have been at least partially dehydrated and/or melted during their subduction. The water content of the residue would depend on the degree of melting, because H is an incompatible element, with partition coefficients similar to that of Ce during the melting (Peslier, et al. 2012), and is easily partitioned into the melt. Type IIB omphacite is more depleted in Ce than Type IIA (0.07 vs 0.18 ppm). Therefore, if the protoliths of

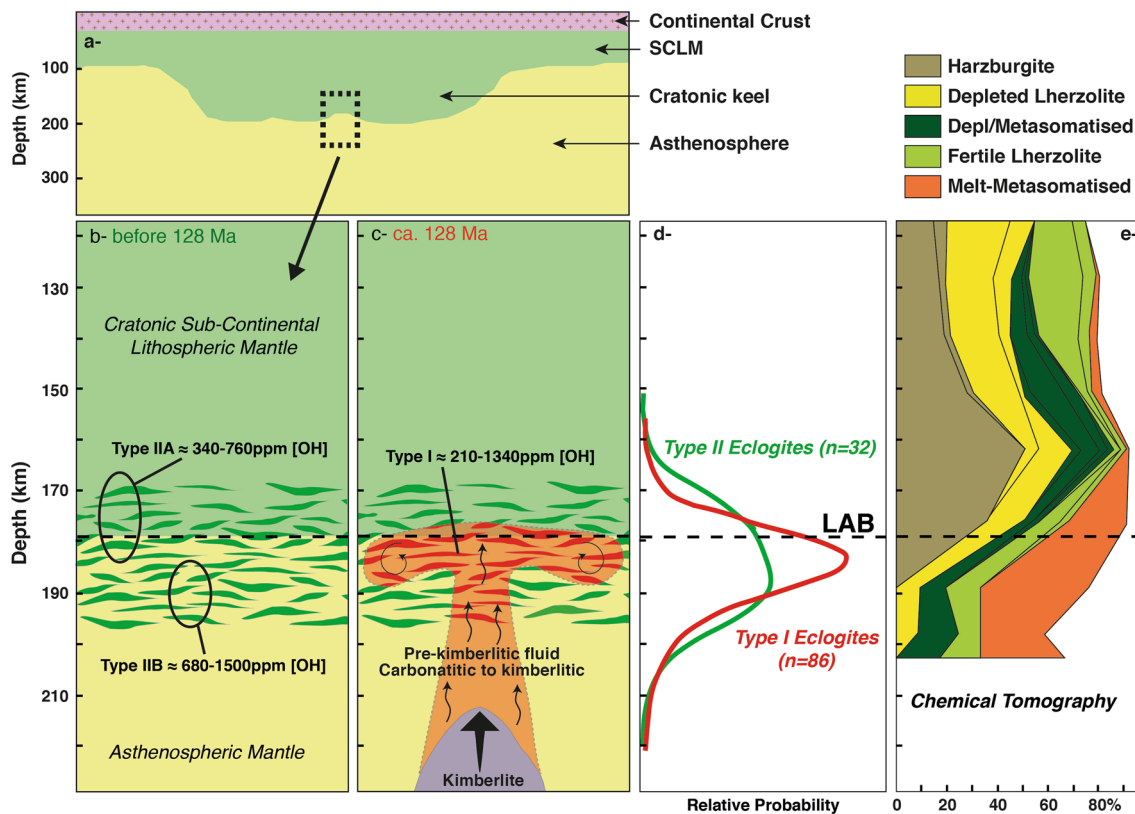


Fig. 4 Cartoon of eclogite-rich domain around the lithosphere-asthenosphere boundary in the Roberts Victor area, South Africa: (a) Schematic structure of the continental crust and upper mantle; (b) Distribution of Type IIA and IIB eclogites in the subcontinental lithospheric mantle (SCLM); (c) Formation of Type I eclogites by the

mantle metasomatism of Type II eclogites with carbonatitic-kimberlitic melts/fluids; (d) Distribution of Type I and Type II eclogites in the SCLM; data from Huang et al. (2012a); (e) Chemical tomography section of the SCLM after Griffin and O'Reilly (2007)

Type IIA and IIB eclogites had the same water content, theoretically Type IIB should contain less water than Type IIA, while the reverse is true. If their protoliths contained different amounts of water, which is quite possible as they have different major-element compositions, the water-enriched rocks could still retain higher water contents after subduction.

If Type II eclogites have been modified by secondary processes (e.g., metasomatism and melting) after formation, they could have had different, non-primary water contents. However, Type II eclogites have depleted trace-element patterns, especially the LILE, and such patterns are not likely to be produced by the mantle metasomatism (O'Reilly and Griffin 2012). It is not clear whether any of the Type II eclogites have undergone partial melting after crystallization. If they have, their water contents would reflect this secondary process, although such a model is difficult to reconcile with the relationships between their water content and their major- and trace-element compositions.

Therefore, the present data do not provide unequivocal clues to the primary origins of Type II eclogites. Type IIA and IIB might have different origins and/or have been modified by different secondary processes.

Water contents of xenolithic eclogites and peridotites

Olivine may contain most of the water in upper mantle peridotites, because of its relative abundance, despite its low water content (0–86 ppm), while pyroxenes can contain larger amount of water (150–400 ppm for cpx and 40–250 ppm for opx). The calculated whole-rock water contents of peridotites from typical cratonic and off-craton areas worldwide are 122 ± 54 and 81 ± 40 ppm, respectively (Peslier et al. 2002; Xia et al. 2010; Yu et al. 2011; Peslier et al. 2012).

The water in xenolithic eclogites, as represented by the samples in this study, is mainly stored in omphacite; the garnet generally does not contain measurable OH. The typical garnet/omphacite ratio for Type I Roberts Victor eclogites is about 50:50; the density of garnet and omphacite in each sample has been calculated based on the density of mineral end members (www.EngineeringToolBox.com) and their relative proportions calculated from the electron-probe major-element compositions (Huang et al. 2012a); and the water content of their omphacite ranges from 211 to 1,337 ppm, 656 ppm

on average. Therefore, the mean water content of the eclogites analyzed here is 341 ± 161 ppm, much higher than that recorded for cratonic peridotites in general, but similar to the water content of eclogites (460 ± 30 , 300 ± 20 ppm) without hydrous minerals from the Kokchetav high-pressure metamorphic terrane (Katayama, et al. 2006). If these eclogites were transferred to the deep Earth, which is possible as they are very dense, they would take much water downwards and therefore play an important role in the water cycle. Although Type IIA omphacite contains much less water (342–764 ppm, median 429 ppm) and Type IIB contains much more (675–1,496 ppm, median 972 ppm) than Type I, these only make up ~5 % of the total sampled volume, assuming that the proportion of rocks sampled on the surface reflects that in the source. Therefore, they do not control the water content of the eclogite-rich domain. In a less-metasomatized volume of the lithosphere, Type IIB eclogite could be an important mantle water reservoir because it contains 503 ± 136 ppm of water. Further work on the water content of the xenolithic eclogites from other localities is needed to generate a more global picture. In summary, eclogites are relatively water-enriched compared with the peridotitic mantle. The presence of significant volumes of eclogite in the mantle would promote a more “dynamic” regime.

Conclusions

- (1) In Roberts Victor xenolithic eclogites, water is mainly stored in omphacite, and garnet does not contain measurable OH. The water contents of Type IA, IB, IIA, and IIB omphacite range from 211–1,337 (median 554), 416–1,001 (median 637), 342–764 (median 429), and 675–1,496 (median 972) ppm, respectively.
- (2) The OH content of the omphacite was not disturbed by interaction with the host magma. No amphibole contributes to the OH measurement of omphacite. While it is possible that some sheet silicates (e.g., clinocllore and amesite) affect one small OH band of omphacite, this would not change the results significantly.
- (3) The crystal chemistry and structure of omphacite and the H₂O fugacity may control the OH content of Type I eclogites. The OH content of Type II samples may be more sensitive to the ^{IV}Al³⁺ content, the equilibrium temperature/pressure, and local fugacities of H₂O and O₂.
- (4) Metasomatism has modified the water contents of the Type I xenolithic eclogites; the samples have been in equilibrium with carbonatitic–kimberlitic melts/fluids rich in water.
- (5) Roberts Victor eclogites contain on average 341 ± 161 ppm water, much more than found in mantle peridotites. Eclogites therefore may be an important water reservoir in specific parts of the mantle, especially near the lithosphere–asthenosphere boundary. This may be an important consideration in geodynamic modeling and in the interpretation of seismic and electrical conductivity data.

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Appendix: Elemental compositions of garnet and cpx of some critical Roberts Victor Type II eclogites

See Table 3.

Table 3 Element compositions (wt%/ppm) of Roberts Victor eclogitic garnets and clinopyroxenes

	HRV58-2		HRV345b		HRV?b		HRV344		HRV175-2		HRV316-2	
Type	IIA		IIA		IIA		IIA		IIB		IIB	
Temp. (°)	963		911		926		928		1,141		1,228	
Depth (km)	173		169		170		170		186		193	
Garnet												
Analysis grain No.	3	1SD	4	1SD	4	1SD	9	1SD	5	1SD	5	1SD
SiO ₂	40.56	0.16	40.44	0.14	40.49	0.15	40.22	0.12	39.43	0.08	39.64	0.12
TiO ₂	0.16	0.01	0.15	0.01	0.16	0.02	0.15	0.03	0.16	0.02	0.16	0.03
Al ₂ O ₃	21.70	0.06	22.79	0.05	22.79	0.09	22.25	0.06	21.27	0.13	21.27	0.08
Cr ₂ O ₃	0.09	0.01	0.16	0.02	0.16	0.01	0.14	0.03	0.08	0.01	0.04	0.03
FeO	19.64	0.30	17.61	0.15	17.54	0.14	16.80	0.11	19.40	0.19	17.02	0.17
MnO	0.37	0.03	0.40	0.02	0.38	0.02	0.38	0.02	0.46	0.02	0.43	0.04
MgO	13.53	0.09	14.11	0.15	14.16	0.07	13.53	0.10	8.92	0.12	8.56	0.06
CaO	4.20	0.16	4.56	0.19	4.47	0.18	5.43	0.17	9.70	0.24	12.09	0.09
Na ₂ O	0.03	0.01	0.04	0.00	0.04	0.01	0.04	0.01	0.05	0.01	0.05	0.01
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
NiO	0.00	0.00	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02
Total	100.28		100.29		100.22		98.95		99.48		99.30	
Clinopyroxene												
Analysis grain No.	5	1SD	3	1SD	6	1SD	5	1SD	3	1SD	5	1SD
SiO ₂	54.86	0.18	54.80	0.58	55.20	0.14	55.50	0.28	54.44	0.11	54.77	0.21
TiO ₂	0.12	0.02	0.19	0.01	0.17	0.01	0.18	0.03	0.20	0.01	0.19	0.01
Al ₂ O ₃	4.31	0.07	6.88	0.15	7.23	0.14	7.28	0.28	8.56	0.25	9.82	0.16
Cr ₂ O ₃	0.07	0.02	0.17	0.02	0.15	0.02	0.14	0.03	0.07	0.01	0.03	0.01
FeO	6.38	0.12	4.43	0.24	4.52	0.21	3.89	0.10	5.76	0.16	4.98	0.10
MnO	0.07	0.03	0.06	0.00	0.08	0.01	0.06	0.01	0.03	0.03	0.04	0.02
MgO	13.18	0.04	12.34	0.12	12.18	0.13	11.71	0.22	9.61	0.23	9.02	0.09
CaO	17.28	0.23	16.17	0.33	15.85	0.25	16.24	0.34	15.61	0.08	15.08	0.17
Na ₂ O	3.28	0.11	4.21	0.07	4.34	0.05	4.26	0.13	4.94	0.06	5.36	0.07
K ₂ O	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
NiO	0.07	0.01	0.03	0.01	0.04	0.01	0.05	0.03	0.02	0.02	0.06	0.02
Total	99.62		99.30		99.76		99.31		99.24		99.36	
Sr ppm	48		27		27		31		18		39	
Nd ppm	0.79		0.85		0.82		0.86		0.40		0.92	

The analysis was carried out at GEMOC, Macquarie University

The methodologies are the same with those given in Huang et al. (2012a)

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