Contrasting oxygen isotopes in garnet from diamondiferous and barren eclogitic parageneses

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Supplementary Information

The Supplementary Information includes:

- Analytical Methods
- Samples and Results
- Supplementary Tables S-1 to S-5
- Supplementary Figures S-1 to S-4
- References for Figures 1, S-3 and S-4, and Table S-2
- References for Figure 2
- Supplementary Information References

Analytical Methods

Diamond Polishing

Diamond inclusions (DIs) were analysed on polished diamond surfaces in situ. Host diamonds have been polished at the Department of Earth, Ocean and Atmospheric Sciences (EOAS) of the University of British Columbia (Vancouver, Canada) using a steel scaif impregnated with diamond powder. No natural or synthetic abrasive material was used for polishing.

Major-element Compositions of the Cullinan DIs: Microprobe Analysis

Major element composition of the exposed inclusions was analysed on a CAMECA SX-50 electron microprobe at EOAS, UBC. The studied samples were coated with carbon, analysed with a beam current of 20 nA, an acceleration voltage of 15 kV, and a peak count time of 20 s (except for K in pyroxene [40 s] and Na in garnet [60 s]); two backgrounds on either side of the peak were counted for 10 s (except for K in pyroxene [20 s] and Na in garnet [30 s]). The diameter of the electron beam was ~5 μm. The following standards, X-ray lines and crystals were used for garnet: albite, Na Kα, TAP; pyrope, Mg Kα, TAP; pyrope, Al Kα, TAP; pyrope, Si Kα, TAP; pyrope, Ca Kα, PET. For the elements considered in pyroxene analyses, the following standards, X-ray lines and crystals were used: albite, Na Kα, TAP; kyanite, Al Kα, TAP; diopside, Mg Kα, TAP; diopside, Si Kα, TAP; orthoclase, K Kα, PET; diopside, Ca Kα, PET; rutile, Ti Kα, PET; synthetic magnesiochromite, Cr Kα, LIF; synthetic rhodonite, Mn Kα, LIF; synthetic fayalite, Fe Kα, LIF. The 'PAP' φ(pZ) method (Pouchou and Pichoir, 1991) has been applied for the data reduction. Detection limits
are given in Table S-1. Fe\(^{3+}\) content was calculated stoichiometrically on the basis of the ideal oxygen unit total for each respective mineral. Chemical compositions of the studied inclusions and related information are given in Table S-5.

**Table S-1** Calculated minimum detection limits in wt. % (MDL) for the Cullinan diamond inclusions.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Grt</th>
<th>Cpx</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>FeO</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>MnO</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>MgO</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>-</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Raman Spectroscopy of the Cullinan DIs**

Raman spectra of the mineral inclusions from diamonds were obtained with a Horiba XploRA PLUS confocal Raman spectrometer equipped with a CCD-detector at EOAS, UBC (Vancouver, Canada). Spectra have been collected at room temperature with the 532.18 nm line of a 14 mW Nd-YAG laser through an OLYMPUS TM 100X objective in the range between 100 and 1500–1800 cm\(^{-1}\) at 1.3 cm\(^{-1}\) spectral resolution, and ~1 μm spatial resolution. The aperture of the confocal hole was set to 200 μm, the spectra slit width was 300 μm.

**Oxygen Isotope Compositions of the Cullinan DIs: Secondary Ion Mass Spectrometry (SIMS)**

Oxygen isotope composition was measured in 50 eclogitic garnet and majorite inclusions (Table S-5).

Preparation of mounts and SIMS study of the samples were conducted at the Canadian Centre for Isotopic Microanalysis (CCIM), University of Alberta. Polished diamonds with the exposed majorite and garnet inclusions were arrayed on a tape and cast in 25 mm diameter epoxy mounts (M1612, M1613) along with CCIM garnet reference materials (RMs) S0068 (Gore Mountain Ca-Mg-Fe garnet), and S0088B (grossularite). The prepared mounts were cleaned with a lab soap solution and de-ionised H\(_2\)O. The studied samples were coated with 25 nm of high-purity Au prior to scanning electron microscopy (SEM). The SEM observations were made with a Zeiss EVO MA15 electron microscope using beam conditions of 20 kV and 3–4 nA. Coating of 100 nm of Au was subsequently deposited on the mount before SIMS analysis.

The oxygen isotope analysis (\(^{18}\)O, \(^{16}\)O) of garnets was conducted using a Cameca IMS 1280 multicollector ion microprobe. Garnet analytical methods and RMs are reported in detail by Ickert and Stern (2013). A \(^{133}\)Cs\(^+\) primary beam was operated with impact energy of 20 keV, and beam current of ~2.0 nA. The probe with the diameter of ~8 μm was rastered (20 × 20 μm) for 30 s prior to acquisition, and then 3 × 3 μm during acquisition, forming elliptical analysed areas ~12 μm across and ~1 μm deep. The normal incidence electron gun was utilised for charge compensation. Negative secondary ions were extracted through 10 kV potential into the secondary (Transfer) column. Transfer conditions
included a 122 µm entrance slit, a 5 × 5 mm pre-ESA (field) aperture, and 133× sample magnification at the field aperture, transmitting all regions of the sputtered area. The mass/charge separated oxygen ions were detected simultaneously in Faraday cups L’2 (16O⁻) and H’2 (18O⁻) at mass resolutions (m/Δm at 10 %) of 1950 and 2250, respectively. Secondary ion count rates for 16O⁻ and 18O⁻ were typically 2 × 10⁹ and 4 × 10⁶ counts/s utilising 10¹⁰ Ω and 10¹¹ Ω amplifier circuits, respectively. Faraday cup baselines were measured at the start of the analytical session. A single analysis took 240 s, including pre-analysis primary beam implantation, automated secondary ion tuning, and 75 s of continuous peak counting.

Instrumental mass fractionation (IMF) was monitored by repeated analysis of S0068 (UAG) and S0088B with δ¹⁸O_VSMOW = +5.72 ‰ and +4.13 ‰, respectively. One analysis of S0068 was taken after every four measurements, and one analysis of S0088B was taken after every eight unknowns. The data set of 18O/16O for S0068 garnet was processed collectively for two analytical sessions, yielding standard deviations of 0.10–0.13 ‰ after correction for systematic within-session drift. Data for S0088B and unknowns were first IMF corrected to S0068 garnet, and then further corrected according to their measured Ca#'s (Ca/ [Ca + Mg + Fe]) using the methods suggested by Ickert and Stern (2013). The quadratic matrix calibration curve parameters (Ickert and Stern, 2013) were scaled to fit S0088B to its reference value. The 95 % confidence uncertainty estimates for δ¹⁸O_VSMOW for garnet unknowns average ±0.30 ‰, and include errors relating to within-spot counting statistics, between-spot (geometric) effects, correction for instrumental mass fractionation, and matrix effects relating to Ca#s determined by electron microprobe wavelength dispersive spectrometry.

All ¹⁸O/¹⁶O ratios are reported in per mil (%) and expressed in delta notation (δ¹⁸O) relative to Vienna Standard Mean Ocean Water (VSMOW) (Baertschi, 1976) in Equation S-1:

\[
\delta^{18}O (\%) = \left[ \frac{({^{18}O}/^{16}O)_{\text{sample}}}{({^{18}O}/^{16}O)_{\text{VSMOW}}} \right] - 1
\]  
(Eq. S-1)

Because the study jointly uses δ¹⁸O values from SIMS and older laser fluorination analyses, it is important to establish their consistency. New data for Roberts Victor eclogitic garnet (Hardman et al., 2021) (Fig. S-1) demonstrate that O isotope measurements by SIMS at the Canadian Centre for Isotopic Microanalysis (CCIM) and laser fluorination (LF) techniques are reproducible with the maximal discrepancy of ±0.35 ‰.

Figure S-1 Reproducibility test for O isotope measurements by SIMS at the Canadian Centre for Isotopic Microanalysis (CCIM), University of Alberta and laser fluorination (LF) techniques for garnet in Roberts Victor eclogites (Hardman et al., 2021).
Samples and Results

Mineral Inclusions from the Cullinan Diamonds

We studied DI in mafic mineral parageneses (eclogitic and majorite-bearing parageneses of the transition zone) from diamonds of the Cullinan mine (Premier kimberlite), South Africa. This location was chosen because its slab-related diamonds formed from the single carbon source with narrow C isotope composition ($\delta^{13}$C of 45 samples = $-1.3$ to $-7.8$ ‰), but derive from a wide interval of pressures ($P$) and temperatures ($T$) (Korolev et al., 2018a, 2018b). Mineral inclusions come from depths of ~170–220 km (Grt and Cpx), 280–420 km (majorites) (Korolev et al., 2018a, 2018b) and >550 km (CaSi-perovskite) (Nestola et al., 2018), covering the broad $T$ range in the lithospheric mantle from 1280 °C up to super-adiabatic 1570 °C (5.6–7.2 GPa) (Korolev et al., 2018a, 2018b). To extend these intervals, we screened the Cullinan diamonds for more coexisting Grt-Cpx pairs and majorites that make the diamonds amenable to thermobarometry. As a result, we analysed 42 Grt-Cpx pairs and 8 majorites and calculated their $P$-$T$s of formation. This number of analyses and their respective $P$-$T$s are the highest reported for eclogitic diamonds from a single kimberlite. The inclusions were analysed for major elements; 50 garnets and majorites were further analysed for oxygen isotopes.

Analysed $\delta^{18}$O compositions of garnet cover a range of +5.4 to +10.2 ‰ that includes the oxygen isotope composition of majorites (+6.0 to +9.4 ‰, Table S-5), indicating that the oxygen isotope composition does not change during slab transfer from the lithospheric to the sublithospheric mantle. Garnets and majorites show no correlation of the O isotopes with $T$ or $P$, except a small subset of Mg-rich garnets coexisting with Cpx low in jadeitic component (Figs. S-2a and S-3).

Covariations of $\delta^{18}$O with Thermodynamic Parameters of DIs

$\delta^{18}$O shows a bimodal distribution with the first peak of around +6.0 ‰ and the other at +8.4 ‰ (green line on Fig. S-2). Garnets with $\delta^{18}$O > 7.0 ‰ show no correlation of the O isotopes with $T$. Garnets with the lighter O ($\delta^{18}$O < 7.0 ‰) can be divided into two groups, associated with the highly jadeitic (Jd) cpx (Jd > 40 %) or not (Fig. S-2b). MgO content of garnets in association with the high-Jd cpx is lower (7.2–12 wt. %, the median is 10.8 wt. %) than MgO content of the other garnets (9.2–17.4 wt. %, the median is 14.1 wt. %; Table S-5). The Mg-poor garnets associated with high-Jd cpx do not demonstrate a $\delta^{18}$O–$T$ correlation, while Mg-rich garnets coexisting with low-Jd Cpx show a pronounced $\delta^{18}$O–$T$ correlation (PCC = 0.72) (Fig. S-2a). The Mg-poor garnets associated with high-jadeitic Cpx are sourced from a variety of temperatures (Fig. S-2a) and pressures. There is no correlation between $P$ and the oxygen isotope composition of garnets and majorites. Although we did not find any global correlation between $T$ or $P$ and $\delta^{18}$O in garnet, the $\delta^{18}$O–$T$ correlation is observed for Mg-rich garnets coexisting with low-Jd Cpx (Fig. S-2a). This correlation, along with analogous data on the Orapa and Lace mantle eclogite xenoliths (Deines et al., 1991; Aulbach et al., 2017) point to occasional presence of correlations restricted to a subset of samples (14 Cullinan inclusions (Fig. S-2a), 13 Lace eclogites (Aulbach et al., 2017), and 12 Orapa eclogites (Deines et al., 1991)). Notably, the $\delta^{18}$O–$T$ correlation relates to the chemical composition of the Cullinan DIs, but also occurs in samples with $\delta^{18}$O < 7 ‰ (Fig. S-2a).
Figure S-2  Covariations of the oxygen isotope compositions for garnets in studied Cullinan diamonds with (a) calculated Cpx-Grt DI temperatures (Nakamura, 2009; adiabat after Katsura et al., 2010) and (b) jadeitic content of the coexisting DI Cpx. Here and on figures below the beige colour strip is the $\delta^{18}$O mantle value canonical mantle range ($5.5 \pm 0.4 \%$) (Mattey et al., 1994). PCC stands for the Pearson Correlation Coefficient.
Figure S-3  Covariations of the oxygen isotope compositions with temperature and pressure for eclogitic Kaapvaal garnets in comparison with the studied Cullinan diamonds. (a) The garnet $\delta^{18}$O vs. calculated Cpx-Grt temperatures (Nakamura, 2009). The temperatures for Kaapvaal eclogite xenoliths (see the database in Table S-5) were recalculated (Nakamura, 2009) for consistency; adiabat is after Katsura et al. (2010). (b) The $\delta^{18}$O vs. estimated $P$. The pressure for Kaapvaal eclogites and Cullinan DIs is calculated by projection of the Cpx-Grt temperatures (Nakamura, 2009) onto the peridotitic geotherm as detailed in Korolev et al. (2018b). Full list of references on major element analyses of Cpx and Grt, and $\delta^{18}$O in garnet is given below. The graphite-diamond phase boundary (Day, 2012) is shown by the blue line. It is positioned for the Kaapvaal craton at the intersection with the 40 mW/m$^2$ model conductive geotherm (Hasterok and Chapman, 2011).
Figure S-4  Covariation between temperature and δ¹⁸O composition for garnet and clinopyroxene from eclogite xenoliths worldwide. (a) The difference in oxygen isotope composition between garnet and clinopyroxene vs. temperature for 181 pairs; the difference between δ¹⁸O_grt and δ¹⁸O_cpx is ±0.87 ‰ (2σ; green area). (b) A plot of δ¹⁸O_grt vs. T. (c) A plot of δ¹⁸O_grt vs. pressure. The full list of references is given below.
Oxygen isotope composition of Cullinan majorites vs. DI majorites worldwide

All majorites that occur as diamond inclusions show relatively high δ¹⁸O values well above the conventional mantle range (Fig. 3). The analysed majorites from Figure 3 include the Cullinan samples presented in this study (7 samples), DI from Jagersfontein (11 samples, Ickert et al., 2015), Juina-5 (3 samples, Burnham et al., 2015), and Collier-4 (3 samples, Burnham et al., 2015) diamonds. Majorites from Cullinan diamonds are notable because of their contrasting O isotope signatures. Majorites with heavy oxygen (δ¹⁸O > 8.7 ‰) comprise 78 % of samples from Jagersfontein, Juina, and Collier, but never found among Cullinan majorites (Fig. 3). Moreover, three Cullinan samples with the lowest δ¹⁸O of 6.0, 6.6, and 7.0 ‰ are not matched by majorites from other locations (Fig. 3 and Table S-5). Majorite DIs from elsewhere may have formed from heavier, hydrothermally altered O source and were found in diamonds with the lighter δ¹³C signatures sourced from organic matter or altered oceanic crust (−26 to −9 ‰, Fig. 3). In contrast, Cullinan majorite inclusions have been captured by diamonds with the mantle δ¹³C signatures (−4.7 to −2.1 ‰, Fig. 3 and Table S-5). This pattern suggests an exclusively shallow crustal source of C and O for majorite-bearing diamonds from Jagersfontein, Juina, and Collier, while the oxygen isotope composition of Cullinan majorites possesses crustal signatures, and host diamonds show prominent affinity with mantle source of carbon. Diamond formation processes in the majorite-hosting diamonds locations were clearly different even though all the majorites formed in the deeply subducted mafic slab and had low-Cr eclogitic major element compositions.

Statistical t-test for δ¹⁸O in Garnets from Diamondiferous and Barren Eclogites from the Kaapvaal Craton

We carried out the independent two-sample unequal t-test for the diamondiferous and barren eclogites from the Kaapvaal craton (Table S-2). The t-test determines that the average δ¹⁸O and its distribution in garnet from the diamondiferous eclogites are distinct from the barren eclogites from the Kaapvaal craton with a probability >99.99 % (Table S-2).

Table S-2   Comparison of the garnet oxygen isotope composition (δ¹⁸O in ‰) in the statistical samples of diamondiferous and barren eclogites from the Kaapvaal craton (data set: full list of references is given below).

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>δ¹⁸O in garnet Diamondiferous eclogites 42</th>
<th>δ¹⁸O in garnet Barren eclogites 187</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average δ¹⁸O (in ‰)</td>
<td>7.28</td>
<td>5.04</td>
</tr>
<tr>
<td>1σ</td>
<td>1.31</td>
<td>1.49</td>
</tr>
<tr>
<td>t-test (calc.)</td>
<td></td>
<td>9.77</td>
</tr>
<tr>
<td>Significance level:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01 %</td>
<td></td>
<td>4.13</td>
</tr>
<tr>
<td>0.1 %</td>
<td></td>
<td>3.44</td>
</tr>
<tr>
<td>1 %</td>
<td></td>
<td>2.65</td>
</tr>
</tbody>
</table>
Geochemical Modelling of $\delta^{18}O$ and $\delta^{13}C$ Effects of Decarbonation Reactions

Numerical modelling of decarbonation at temperatures 1000 and 1200 °C was carried out for the following reactions also listed in Table S-4:

1. $\text{Alm} + 3 \cdot \text{Mgs} = \text{Prp} + \text{Mag} + 3 \cdot \text{C} + 2.5 \cdot \text{O}_2$
2. $2 \cdot \text{Grt} + 2 \cdot \text{Tmn} + 2 \cdot \text{Mgs} = 2 \cdot \text{Grt} + \text{Cpx} + 2 \cdot \text{Ilm} + 2 \cdot \text{C} + 2 \cdot \text{O}_2$
3. $2 \cdot \text{Grt} + 2 \cdot \text{Tmn} + 2 \cdot \text{Mgs} = 2 \cdot \text{Grt} + \text{Cpx} + 2 \cdot \text{Ilm} + 2 \cdot \text{CO}_2$
4. $\text{Prp} + \text{Rt} + \text{Mgs} = \text{Mg-Prp} + \text{Gk} + \text{CO}_2$
5. $\text{Prp} + 2 \cdot \text{Qz} + \text{Dol} = \text{Prp} + \text{Di} + 2 \cdot \text{CO}_2$
6. $3 \cdot \text{Prp} + 4 \cdot \text{Qz} + 2 \cdot \text{Mgs} = 2 \cdot \text{Prp} + 4 \cdot \text{En} + 2 \cdot \text{Ky} + 2 \cdot \text{CO}_2$
7. $\text{Grs} + \text{Di} + 2 \cdot \text{Qz} + \text{Dol} = \text{Grs} + 2 \cdot \text{Di} + 2 \cdot \text{CO}_2$

All phases except $\text{O}_2$ in the proposed reactions are found in cratonic eclogites (e.g., Jacob, 2004; Smith et al., 2015; Mikhailenko et al., 2022), and some of them are one of several end members of more complex mineral composition (Di and En as a component of omphacite eclogitic Cpx; Alm, Grs, and Prp are components of a more complex Grt composition). Quartz substitutes for coesite for the purpose of $\delta^{18}O$ modelling. As can be seen from reactions 1 and 2 above, they produce $\text{O}_2$, which we treat as a virtual component, not as a free gas phase in the deep mantle. The oxygen oxidises garnet and clinopyroxene, for example in reaction (8a):

$$\text{8a. } 2 \cdot (\text{Fe}^{2+}1.2:1.3\text{Mg}_{0.02}\text{Ca}_{0.25})_{1.00} \cdot \text{Al}_{2.00} [\text{SiO}_4]_3 + 8 \cdot (\text{Ca}_{0.20}\text{Na}_{0.80})_{1.00} (\text{Mg}_{0.02}\text{Al}_{0.08})_{1.00} (\text{Si}_2\text{O}_6) + 5.5 \cdot (\text{Ca}_{0.90}\text{Na}_{0.10})_{1.00} (\text{Mg}_{0.82}\text{Fe}^{3+}_{0.08}\text{Al}_{0.10})_{1.00} (\text{Si}_2\text{O}_6) + 0.5 \cdot \text{O}_2$$

$$= 3 \cdot (\text{Mg}_{1.10}\text{Ca}_{1.00}\text{Fe}^{2+}_{0.00})_{1.00} (\text{Al}_{1.00}\text{Fe}^{3+}_{0.02})_{1.00} [\text{SiO}_4]_3 + 10 \cdot (\text{Ca}_{0.35}\text{Na}_{0.65})_{1.00} (\text{Mg}_{0.35}\text{Al}_{0.46}\text{Fe}^{3+}_{0.19})_{1.00} (\text{Si}_2\text{O}_6) + (\text{Ca}_{0.55}\text{Na}_{0.45})_{1.00} (\text{Mg}_{0.55}\text{Al}_{0.41}\text{Fe}_{0.04})_{1.00} (\text{Si}_2\text{O}_6) + 2 \cdot \text{SiO}_2.$$

Compositions of garnet and clinopyroxene in the reaction are taken from natural eclogite samples where mineral $\text{Fe}^{3+}$ are analysed (Kopylova et al., 2016; Aulbach et al., 2022). For the purposes of oxygen isotope modelling, the reaction is simplified as:

$$\text{8b. } 2 \cdot \text{Grt} + 13.5 \cdot \text{Cpx} + 0.5 \cdot \text{O}_2 = 3 \cdot \text{Grt} + 11 \cdot \text{Cpx} + 2 \cdot \text{Qz( stable)}.$$

Reactions (1–8) are fully balanced. We assumed the initial equilibrium of all reactants with garnet with $\delta^{18}O = +6$‰. The modelling used oxygen and carbon fractionation factors derived from isotope equilibration of silicate minerals with carbonate, of CO$_2$ and O$_2$ and applicable to high temperatures of the lithospheric mantle (Table S-3). We also calculated relevant oxygen isotope fractionation factors (Table S-3) from the internally consistent database of Vho et al. (2019) at 1000 and 1200 °C. For reaction 8 that involves oxidation, we used O$_2$ with a range of $\delta^{18}O$ values calculated from reactions (1) and (2); net effects for combined reactions (1) + (8) and (2) + (8) are also listed (Table S-4).
## Table S-3  Fractionation of oxygen isotopes in the modelled decarbonation reactions at 1000 and 1200 °C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>10$^3$$\ln\alpha$ at 1000 °C</th>
<th>10$^3$$\ln\alpha$ at 1200 °C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alm–Mag</td>
<td>2.23</td>
<td>1.85</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Alm–Mgs</td>
<td>−2.28</td>
<td>−1.91</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Grs–Di</td>
<td>−0.34</td>
<td>−0.27</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Grs–Dol</td>
<td>−2.36</td>
<td>−1.96</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Grs–Qz</td>
<td>−2.35</td>
<td>−1.93</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Grt–Cpx</td>
<td>0.02</td>
<td>0.02</td>
<td>Chacko et al. (2001)</td>
</tr>
<tr>
<td>Grt–Mag</td>
<td>2.21</td>
<td>1.65</td>
<td>Chacko et al. (2001)</td>
</tr>
<tr>
<td>Grt–Ttn</td>
<td>0.59</td>
<td>0.44</td>
<td>Chacko et al. (2001)</td>
</tr>
<tr>
<td>Jd–Prp</td>
<td>1.36</td>
<td>1.14</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Jd–Qz(Coe)</td>
<td>−1.24</td>
<td>−1.03</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Mgs–CO$_2$</td>
<td>1.86</td>
<td>1.43</td>
<td>Chacko and Deines (2008)</td>
</tr>
<tr>
<td>Prp–Dol</td>
<td>−2.62</td>
<td>−2.20</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–En</td>
<td>−0.39</td>
<td>−0.31</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Gk</td>
<td>2.39</td>
<td>1.98</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Ilm</td>
<td>2.13</td>
<td>1.76</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Jd</td>
<td>−1.36</td>
<td>−1.14</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Ky</td>
<td>0.89</td>
<td>0.71</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Mgs</td>
<td>−2.54</td>
<td>−2.13</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Qz</td>
<td>−2.61</td>
<td>−2.17</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Rt</td>
<td>1.21</td>
<td>1.02</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Prp–Ttn</td>
<td>−0.06</td>
<td>−0.04</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Qz–Dol</td>
<td>−0.02</td>
<td>−0.03</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
<tr>
<td>Qz–Mgs</td>
<td>−0.02</td>
<td>−0.03</td>
<td>Calculated from database of Vho et al. (2019)</td>
</tr>
</tbody>
</table>

Mineral abbreviations (according to Warr, 2021): Alm, Almandine; Coe, coesite; Cpx, clinopyroxene; Di, diopside; Dol, dolomite; En, enstatite; Gk, geikielite; Grs, grossular; Grt, garnet; Ilm, ilmenite; Jd, jadeite; Ky, kyanite; Mag, magnetite; Mgs, magnesite; Prp, pyrope; Rt, rutile; Qz, quartz; Ttn, titanite.
Table S-4  \( \delta^{18}\text{O} \) effects for reactions of diamond formation

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Reactions</th>
<th>( \delta^{18}\text{O} ) effect on the resulting Grt (‰) as the reaction proceeds at 1000 °C</th>
<th>at 1200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alm + 3·Mgs = Prp + Mag + 3·C + 2.5·O$_2$</td>
<td>1.3–1.4</td>
<td>1.0–1.1</td>
</tr>
<tr>
<td>2</td>
<td>2·Grt + 2·Ttn + 2·Mgs = 2·Grt + Cpx + 2·Ilm + 2·C + 2·O$_2$</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>2·Grt + 2·Ttn + 2·Mgs = 2·Grt + Cpx + 2·Ilm + 2·CO$_2$</td>
<td>0.1–0.3</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>4</td>
<td>Prp + Rt + Mgs = Mg-Prp + Gk + CO$_2$</td>
<td>0.03–0.2</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>5</td>
<td>Prp + 2·Qz +Dol = Prp + Di + 2·CO$_2$</td>
<td>0.1–0.5</td>
<td>0.2–0.4</td>
</tr>
<tr>
<td>6</td>
<td>3·Prp + 4·Qz + 2·Mgs = 2·Prp + 4·En + 2·Ky + 2·CO$_2$</td>
<td>0.5–0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>Grs + Di + 2·Qz + Dol = Grs + 2·Di + 2·CO$_2$</td>
<td>−1.6 to −1.4</td>
<td>−1.6 to −1.4</td>
</tr>
<tr>
<td>8</td>
<td>2·Grt + 13.5·Cpx + 0.5·O$_2$ = 3·Grt + 11·Cpx + 2·Qz(Coe)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(1) + (8)  Net effect for (8) taking place after (1)  1.4–1.5           1.1–1.2
(2) + (8)  Net effect for (8) taking place after (2)  0.7                0.6

Calculations are done for \( \delta^{18}\text{O} \) of the Grt/Alm reactant of 6 ‰ and \( \delta^{13}\text{C} \) of Mgs reactant of −6 ‰. Abbreviations of minerals (according to Warr, 2021): Alm, almandine; Cpx, clinopyroxene; Di, diopside; Dol, dolomite; En, enstatite; Gk, geikielite; Grs, grossular; Grt, garnet; Ilm, ilmenite; Jd, jadeite; Ky, kyanite; Mag, magnetite; Mgs, magnesite; Prp, pyrope; Rt, rutile; Qz, quartz; Ttn, titanite.

The decarbonation was considered as a Rayleigh process in accordance with (Baumgartner and Valley, 2001), where the O isotope composition of the metasomatic agent is described as:

\[
\delta_{\text{Mgs}} = 10^3[f^{a-1} - 1] \quad \text{(Eq. S-2)}
\]
where $\delta_{\text{Mgs}}$ – oxygen isotope composition of magnesite at any stage of the decarbonation; $f$ – the extent to which the decarbonation reaction proceeds, or an abundance of oxygen in the carbonate residue; $\alpha$ – the fractionation coefficient of oxygen isotopes in the CO$_2$-Mgs (O$_2$-Mgs) system.

For any state of the system characterised by value $f$, the following equation calculates $\delta^{18}$O of CO$_2$ or O$_2$:

$$\delta_{\text{fluid}} = (\delta^{18}_{\text{Mgs}} - f \cdot \delta_{\text{Mgs}})/(1 - f)$$  \hspace{1cm} (Eq. S-3)

The oxygen isotope composition of the reaction products (for example, newly formed garnet and magnetite in Reaction 1) can be calculated using mass balance:

$$\delta_{\text{Prp}} = \frac{\delta_{\text{tot}} - \delta_{\text{O2}} \cdot X_{\text{O2}} + \Delta_{\text{Grt-Mag}} \cdot X_{\text{Mag}}}{X_{\text{Grt}} + X_{\text{Mag}}}$$  \hspace{1cm} (Eq. S-4)

where $\delta_{\text{Prp}}$ – oxygen isotope composition of the newly-formed pyrope; $\delta_{\text{O2}}$ – oxygen isotope composition of the product fluid phase; $\Delta_{\text{Grt-Mag}}$ – equilibrium oxygen isotope fractionation between garnet and magnetite; $X_{\text{O2}}$, $X_{\text{Grt}}$, and $X_{\text{Mag}}$ – molar fractions of the reaction products oxygen, garnet, and magnetite, respectively; $\delta_{\text{tot}}$ – oxygen isotope composition of the whole (total) system.

All of the above reactions are applicable to majorite formation in the sublithospheric mantle. Carbonatitic fluids traverse the transition zone and the lower mantle (Collerson et al., 2010; Timmerman et al., 2021) as evidenced by micron-sized carbonate inclusions in sublithospheric diamonds (Kaminsky et al., 2016; Zedgenizov et al., 2016). Clinopyroxene (diopside) is stable in the transition zone to depths of ~570 km (17–18 GPa; Canil, 1994), while ilmenite is stable down to 20–26 GPa, at pressures of the lower mantle (Yu et al., 2011). Ilmenite and magnetite are described as inclusions in sublithospheric diamonds (e.g., Kaminsky et al., 2001, 2009; Kaminsky, 2012). Titanite’s $P$-$T$ stability field as an independent phase and as a solid solution end member extends to the sublithospheric mantle as shown by experiments in the bulk mafic composition (Kanzaki et al., 1991; Gasparik et al., 1994; Knoche et al., 1998). Coesite (quartz in the reactions from Table S-4) can be in equilibrium with majorite in the sublithospheric mantle down to about 10.5 GPa, subsequently in the transition zone it transforms into stishovite (Zhang et al., 1996 and references therein). In the absence of fractionation coefficients for isotopes in majorite, we employed respective coefficients $\Delta_{\text{Grt}}$ for garnet.

**Supplementary Table**

**Table S-5** (Sheet 1) Point-by-point data on oxygen isotope analyses of majorite and garnet inclusions from the Cullinan diamonds measured by SIMS. (Sheet 2) Averaged oxygen isotope and major-element composition (for samples) of majorite and garnet inclusions from the Cullinan diamonds measured by SIMS. (Sheet 3) Averaged major-element composition of the clinopyroxene inclusions from the studied Cullinan diamonds (in wt. %)

Table S-5 (.xlsx) is available for download from the online version of this article at [https://doi.org/10.7185/geochemlet.2328](https://doi.org/10.7185/geochemlet.2328).
References for Figures 1, S-3 and S-4, and Table S-2

The following references were used for compiling Figures 1a and S-3 and Table S-2.

**Cullinan (Premier) diamond inclusions (50 samples)**

This study

**Kaapvaal barren eclogites (187 samples)**


The following references were used for compiling Figures 1b and S-4 and Table S-2.

**Diamondiferous eclogites worldwide (210 samples)**


**Garnet diamond inclusions worldwide (89 samples)**


References for Figure 2

The following references were used for compiling Figure 2.

Barren eclogites


### Diamondiferous eclogites


Supplementary Information References


