Contrasting oxygen isotopes in garnet from diamondiferous and barren eclogitic parageneses

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Abstract

Eclogite is a minor mantle lithology, present in subducted slivers in cratonic roots. Mantle eclogites carry O and C isotopic signatures from surface organic and inorganic carbon and also are modified by reaction with fluids in the lithosphere. One third of the diamonds mined worldwide are sourced from mantle eclogites, and individual eclogite xenoliths contain up to 20 vol. % diamond. It is critically important to understand where the diamond carbon comes from, and how the diamonds form, for insights on the carbon cycle, diamond exploration, and processes in the lithospheric mantle. Few samples and methods are available to constrain diamond formation in eclogites; in this work we focus on oxygen isotopes in eclogitic garnets. New analyses of garnet/majorite found as inclusions in the Cullinan diamonds reveal a statistically significant systematic difference between δ18O in garnet associated, and unassociated, with diamond. This contrast persists between garnet from diamondiferous and barren eclogite xenoliths and cannot be due to shielding of diamond inclusions from equilibrating with the common mantle values of δ18O. We propose that diamond-forming metasomatic reactions triggered by carbonatitic fluids may contribute up to 1.5 ‰ to the shift of δ18O to higher values in eclogitic diamondiferous paragenesis, but cannot fully account for the observed difference of 2.5 ‰.

Introduction

Eclogite, a high grade garnet (Grt)-clinopyroxene (Cpx) rock metamorphosed from the mafic crust, is the most diamondiferous mantle lithology. Diamond concentrations in mantle eclogite can be orders of magnitude higher than the concentration of diamonds in kimberlite – the rock from which they are mined. Over the past 40 years, the oxygen isotope composition (δ18O) of eclogite has become one of the most powerful indicators of its crustal origin in the cratonic mantle (Schulze et al., 2003), together with stable isotopes of C, N and S, and radiogenic isotopes (Pearson et al., 2003; Jacob, 2004). Diamond growth, however, is envisioned as a process overprinting the recycled shallow eclogite protolith. Crustal protoliths for the eclogite do not necessarily imply crustal sources for its diamonds, which could inherit shallow C and O, or could be introduced to the eclogite from mantle fluids. A knowledge of diamond formation in eclogites is critically important to unravel the carbon cycle and deep mantle processes. Diamond formation is considered to be partly metasomatic, as suggested by diamond distribution in eclogites (Taylor and Anand, 2004), δ13C core-to-rim patterns (Smart et al., 2011) and correlations of O isotopes with trace element indicators of metasomatism (Gréau et al., 2011; Huang et al., 2012). Diamond precipitates from mantle C-bearing fluids percolating upward and experiencing Raleigh fractionation (Stachel and Luth, 2015; Riches et al., 2016). Possible effects of metasomatic diamond formation on δ18O of eclogitic minerals may be especially notable for diamondiferous parageneses. Our goal is to quantify these δ18O to separate out the signatures of shallower crustal alteration from the changes introduced from deeper-seated diamondiferous fluids.

It has been noticed that garnet and clinopyroxene in diamondiferous eclogites are higher in δ18O than their respective phases in barren eclogites (Pearson et al., 2003). The difference was explained by the origin of garnet in diamondiferous assemblages from the shallow, more altered part of the oceanic crust where δ18O is higher (McCulloch et al., 1981; Alt et al., 1986; Ickert et al., 2013). This study aims to extend the comparison to eclogitic inclusions in diamonds and make it more statistically robust. In the last 20 years, advances in measurements of O isotopes and new kimberlite discoveries created an abundance of new data. A new summary on δ18O in garnet from diamondiferous and barren parageneses is long overdue. Here we confirm the distinction between δ18O of garnet equilibrated...

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and unequilibrated with diamond and assess how much of this distinction can be assigned to diamond-friendly metasomatism.

## Samples, Methods and Results

We studied diamond inclusions (DIs) from Cullinan Mine (Premier kimberlite) individual raw diamonds. The inclusions are associated with mafic eclogotic and majorite-bearing sublithospheric parageneses. They are derived from a wide interval of temperatures (T) and pressures (P) of 5.5–7.5 GPa from the lithosphere and 10.5–13.5 GPa from the sublithospheric mantle (Korolev et al., 2018a). Here we report major element, δ18O, and P-T data for 42 non-touching Grt-Cpx pairs and 8 majorites (Supplementary Information; Table S-5). Analysed 18O composition of garnet ranges from +5.4 to +10.2 ‰ and covers the oxygen isotope composition of majorites worldwide (+6.0 to +9.4 ‰; Burnham et al., 2015; Ickert et al., 2015).

This new dataset of O isotopes in eclogitic garnet DIs enables statistical comparison with global datasets. The most notable pattern is revealed by a comparison of δ18O in garnet/majorite associated with diamond (DIs and diamondiferous eclogites) and garnet in barren eclogites. Statistical t tests determine that the average δ18O and its distribution in garnet from diamondiferous eclogites are distinctly higher than the barren eclogites from the Kaapvaal craton with probability >99.99 % (Supplementary Information). The δ18O compositions of the garnet/majorite inclusions from the Cullinan diamonds are higher than the δ18O of garnet in Kaapvaal barren eclogites (Fig. 1a). While only 24 % of Cullinan DIs demonstrate δ18O < +6 ‰ and values < +5 ‰ are completely absent (Fig. 1a, Table S-5), 67.4 % of garnets from the barren eclogites have δ18O < +6.0 ‰. Diamondiferous eclogites globally show a narrow δ18O distribution with a higher mode than the Kaapvaal barren eclogites (Fig. 1b).

## Discussion

Several explanations may account for the contrasting δ18O in barren and diamondiferous eclogitic parageneses. The latter may have formed deeper (>150 km), at higher pressures and temperatures. A suggested positive covariation of δ18O with equilibration temperature for Laces eclogites may hint at a wider T–δ18O correlation in the deep mantle as heavy oxygen may favour garnet with increasing T and P (Aublach et al., 2017).

To test for this, we compiled data for eclogite xenoliths of the Kaapvaal craton (Fig. S-3a) and worldwide occurrences (Fig. S-4). The absence of δ18O correlations of garnet DIs with the P-T of their formation observed in Cullinan (Fig. S-3) is repeated globally. A comparison of the δ18O in Grt-Cpx pairs from eclogite xenoliths worldwide equilibrated at the widest range of temperatures (650–1500 °C) shows that there is no dependence between δ18Ogrt or δ18Ocpx and temperature (Fig. S-4). The difference between δ18Ogrt and δ18Ocpx is constant (±0.87 ‰, 2σ) and does not correlate with temperature (Fig. S-4a). The contrasting δ18O compositions in barren and diamondiferous parageneses do not relate to pressure, which was predicted by Clayton et al. (1975). Only a small proportion of Cullinan Mg-rich DIs demonstrate a local δ18O–T correlation (Supplementary Information; Fig. S-2b). Thus, higher pressures and temperatures of diamondiferous eclogites and DIs cannot account for the heavier oxygen in their garnets.

An alternative explanation invokes diffusive buffering of oxygen by the surrounding mantle to explain the δ18O contrast between garnet in barren (xenoliths) and diamondiferous eclogitic parageneses (DIs and xenoliths). DI garnet is shielded from re-equilibration with the ambient mantle oxygen (δ18O = +5.5 ± 0.4 ‰; Mattey et al., 1994), while the “exposed” garnet in xenoliths is not. Only silicate inclusions protected by diamonds retained the δ18O-enriched compositions (Schulze et al., 2003; Burnham et al., 2015; Ickert et al., 2015) formed via low temperature seawater alteration of the shallowest levels of the former oceanic crust (McCulloch et al., 1981; Alt et al., 1986). These diamonds and their mineral inclusions originated from carbon and oxygen derived from the sedimentary organic matter or altered oceanic crust (Li et al., 2019) subducted into the mantle, as evidenced by a correlation of heavy δ18O in silicate DIs and light, low 13C/12C carbon (Ickert et al., 2015; Li et al., 2019). The extent of this “diamond shielding” effect can be evaluated by comparing δ18O histograms for garnet in DIs and diamondiferous eclogites. The δ18O mode for the DI garnet is between +7 and +8 ‰, 1 % higher than the mode for the exposed garnet in diamondiferous eclogites (Fig. 1b).

One cannot defer to the “diamond shielding” effect to explain the contrast between garnet compositions of diamondiferous and barren xenoliths. The latter show a mode at +5 to +6 ‰, at a lower δ18O than diamondiferous xenoliths, and an extended “tail” of the distribution towards 0 ‰ (Fig. 1a). A clear difference in δ18O was shown for both Cpx and Grt for barren and diamondiferous eclogites worldwide (Fig. 2). Traditionally,
this difference would be explained as the contrast in δ18O of the
eclipte protoliths is related to their depth position within the
slab and the gradual decrease of δ18O with depth in the oceanic crust (McCulloch et al., 1981; Alt et al., 1986). In this model, gar-
net in barren eclogites might have inherited the δ18O from deep
gabbrb layers of oceanic crust (δ18O = 0 to +5‰; Alt et al., 1986). Diamoniferous eclogites with higher δ18O, by contrast, may
have recorded a higher input from altered oceanic basaltal
(δ18O = +7 to +15‰; McCulloch et al., 1981; Alt et al., 1986; Eiler, 2001; Korolev et al., 2018b).

The second model can explain light C and heavy O isotope
compositions of many diamonds and their inclusions, where car-
bonate in altered mafic-ultramafic oceanic crust with δ13C = +11 to
+33‰, δ18O = −30 to −5‰ (Li et al., 2019) and organic C (Fig. 3) contributed to eclogite protoliths. Yet the Cullinan
diamonds with eclogite and sublithospheric majoritic inclusions have the characteristic mantle δ13C of −2.4 to −4.8‰ (Fig. 3)
distinguishable from Cullinan peridotitic diamonds (Korolev et al., 2018a). Thus, the model implying contribution of carbonate
in altered mafic-ultramafic oceanic crust cannot be universally
applied to all diamonds with inclensions enriched in heavy O,
although the model adequately explains compositional patterns in
many diamond occurrences.

Another factor that may contribute to contrasting δ18O in
barren and diamoniferous eclogites are diamond-forming
metasomatic reactions. Metasomatism plays a central role in dia-
mond formation (Stachel and Harris, 2008), and its effect on sta-
ble isotopes of diamoniferous parageneses ought to be quantitatively assessed. It was proposed that the metasomatism
may have modified the eclogite protolith by diffusional equil-
ibration with a carbonatic fluid (Lowry et al., 1999) or with the
mantle carbonatic fluids containing heavy oxygen (δ18O of
+5 to +10.5‰) (Gréau et al., 2011; Huang et al., 2016).
However, any fluid deviating from the mantle O isotopic com-
position is expected to be short lived, as it would be buffered back
to the mantle δ18O values by re-equilibration with ambient peri-
dotite oxygen reservoirs (Riches et al., 2016).

We tested viable diamond-forming reactions that do not
involve heavy oxygen-rich fluids for δ18O enrichment effects. Diamond can form by oxidation of methane-rich fluids, by

\[
\text{Almandine } + 3 \cdot \text{Magnetite } = \text{Pyrope } + \text{Magneteit } + 3 \cdot C + 2.5 \cdot O_2
\]

reduction of carbonatitic fluids or by isochemical precipitation
from cooling or ascending C-H-O fluids (Stachel and Luth, 2015). The isochemical precipitation would not shift δ18O, while oxidation of methane or other reduced fluids equilibrated
with H2O would lead to metasomatic silicat with lighter oxygen compositions (Ickert et al., 2013). An origin of diamond
from an oxidised medium was suggested on the basis of the
core-to-rim increases in δ13C composition of individual diamonds (Smart et al., 2011) and daughter minerals in fluid inclu-
sions in diamonds (Kopylova et al., 2010). We modelled δ18O effects for metasomatism by oxidizing fluids in multiple feasible reactions with the realistic eclogite mineralogy. The reactions start with the carbonatic fluid equilibrated with the initial
garnet δ18O of −6.0‰ and leads to a δ18O value of resulting garnet elevated by as much as 1.5‰ (Fig. 4; Supplementary Information). diamond-forming metasomatis-
ing reactions with the strongest δ18O shift upward involve 1) prodution of O2 or CO2, 2) heavy oxygen supplied by the
carbonatic fluid, 3) a sufficiently high fluid/rock ratio (1–3 moles of fluid to 1 mole of garnet), and 4) oxides (rutile or ilmenite) as products rather than reactants. In Reactions 1 and 2 (Table S-4), diamond forms by disproportionation also creating free O2, which is immediately used up to make Fe3+-bearing Grt and Cpx (Reaction 8: Table S-4). Reactions 3–7 (Table S-4) facilitate diamond production indirectly, by
adding carbon dioxide to C-O-H mantle fluids that may be parenatal to diamonds (Stachel et al., 2022). The CO2 concentra-
tions in the mantle, however, are expected to be low, buffered by silicate carbonation (Kopylova et al., 2021). In CO2 produc-
ing reactions the δ18O of product garnet is elevated by 0.5 to
0.6‰ (Table S-4), and the strongest δ18O upward shift of 1.5‰ is observed as a net effect of Reaction 1:

\[
\text{Almandine } + 3 \cdot \text{Magnetite } = \text{Pyrope } + \text{Magneteit } + 3 \cdot C + 2.5 \cdot O_2
\]
followed by Reaction 8:

\[ 2 \cdot \text{Grt} + 13.5 \cdot \text{Cpx} + 0.5 \cdot \text{O}_2 = 3 \cdot \text{Fe}^{3+} \text{-bearing Grt} + 11 \cdot \text{Fe}^{3+} \text{-bearing Cpx} + 2 \cdot \text{Quartz(Coesite)}. \]

All phases in the proposed reactions are found in cratonic eclogites (e.g., Jacob, 2004), and the latter reaction is based on the observed concentrations of Fe\(^{3+}\) in eclogitic minerals (Aulbach et al., 2022). A replacement of eclogitic garnet with a more magnesian garnet has been described in multiple occurrences as part of diamond-friendly metasomatism (e.g., De Stefano et al., 2009; Korolev et al., 2021). An increase of MgO was found to be the most significant chemical change accompanying δ\(^{18}\)O enrichment in garnet from Orapa eclogite xenoliths (Deines et al., 1991). It is well known that metasomatism oxidises the adjacent metasomatised mantle (Creighton et al., 2019). The reactions are equally applicable to majorities in the sublithospheric mantle (Supplementary Information).

We conclude that some metasomatic reactions of diamond formation in eclogites may contribute to the observed δ\(^{18}\)O contrast between barren and diamondiferous eclogite assemblages worldwide, yet the strongest upward δ\(^{18}\)O shift of all feasible metasomatic reactions (up to 1.5 %) achieved in decarbonation followed by metasomatic oxidation is not sufficient to explain the 2.5 % difference in δ\(^{18}\)O (Fig. 4). Inheritance of the O isotopic composition from the crustal eclogitic protoliths is the only model that currently offers a satisfactory explanation for the contrast. This implies preferential diamond formation in eclogites with shallow basaltic protoliths with or without contribution of carbonate in altered mafic-ultramafic oceanic crust that experienced stronger low temperature alteration on the seafloor.

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**Additional Information**

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2328.

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