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The importance of carbon to the formation and compositions of silicates during mantle metasomatism --Manuscript Draft--

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Abstract:	Mineral and fluid inclusions in mantle diamonds provide otherwise inaccessible information concerning the nature of mantle metasomatism and the role of fluids in the mass transfer of material through the Earth's interior. We explore the role of the carbon concentrations during fluid-rock metasomatism in generating the ranges of garnet and clinopyroxene compositions observed in diamonds from the sub-continental lithospheric mantle. We use the Deep Earth Water model to predict the results of metasomatism between silicic, carbonatitic and peridotitic fluids with common mantle rocks (peridotites, eclogites and pyroxenites) at 5 GPa, 1000 °C, across a range of redox conditions ($\log fO_2 = -2$ to $-4 \Delta FMQ$), and a wide range of initial carbon concentrations in the metasomatic fluids. Our results show that the predicted compositions of metasomatic garnets and clinopyroxenes are controlled by the initial compositions of the fluids and the rocks, with subsequent mineral-specific geochemical evolution following definable reaction pathways. Model carbon-rich, metasomatic fluids that can form diamond (initial C- content > 5.0 m) result in Mg-rich garnets and clinopyroxenes typical of peridotitic, eclogitic, and websteritic inclusions in diamonds. However, model carbon-poor, metasomatic fluids that do not form diamond can result in Mg-poor, Ca-rich garnets and clinopyroxenes. Such garnets and clinopyroxenes can nevertheless occur as inclusions in diamonds. In our models, the abundance of carbon in the fluids controls the behaviour of the bivalent ions through the formation of aqueous Mg–Ca–Fe–C complexes which directly govern the composition of garnets and clinopyroxenes precipitated during the metasomatic processes. As the C-rich initial fluids can form the higher Mg-eclogitic, peridotitic, and websteritic inclusions in diamonds, these inclusions can be syngenetic (metasomatic) or possibly protogenetic. However, in our models, the relatively Mg-poor, Ca- and Fe-rich eclogitic garnet and clinopyroxene inclusions found in mantle diamonds formed from C-poor fluids that do not form diamonds. These inclusions most likely reflect a metasomatic event prior to being incorporated into their host diamonds, or they could represent a protolith-based protogenetic geochemistry.
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Earth and Environmental Sciences

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Dear Editor,

Submission of paper to *Geochimica et Cosmochimica Acta*,

We are excited to provide you with a copy of our manuscript entitled “*The importance of carbon to the formation of diamond inclusions*” to be considered for publication in *Geochimica et Cosmochimica Acta*. We believe the manuscript is in line with the aim and scope of *Geochimica et Cosmochimica Acta* and has a broad interest in the geochemical community. This work concerns the origin of silicate inclusions found in mantle diamonds and their geochemical evolution during metasomatic processes. Our work draws attention to how different paragenetic groups can be genetically related and how the amount of carbon in the fluid directly controls their composition.

Our contribution furthers our understanding of diamond inclusion formation and the importance of fluid metasomatism on the petrology of mantle rocks. Diamond inclusions either reflect pre-metasomatic upper mantle heterogeneity and/or metasomatism coeval with diamond formation. We use the Extended Deep Earth Water Model to simulate fluid-rock metasomatism in isothermal and isobaric systems. We focus on the origin of lithospheric garnets and clinopyroxenes at 5 GPa, 1000°C, and across relevant redox conditions for diamond formation ($\log fO_2 = -2$ to -4 ΔFMQ). Our data demonstrate – surprisingly – that the amount of carbon in the fluid plays a primary role in controlling the geochemical composition of silicate minerals through the formation of aqueous Mg–Ca–Fe–C complexes. We posit that pyrope-poor garnet and wollastonite + ferrosillite-rich clinopyroxene inclusions are protogenetic. Thus, their geochemistry should reflect their protolith (eclogite). If so, these samples are incredibly valuable tracers of mantle melting and subduction events through deep time. Conversely, higher Mg-eclogitic, peridotitic, and websteritic inclusions can be either protogenetic (primary) or syngenetic (metasomatic).

We suggest Prof Helen Williams, Prof Raj Dasgupta, or Dr Julie Prytulak, as possible editors for this manuscript due to their expertise in the subjects discussed in this work.

None of the submitted material has been published or is under consideration for publication elsewhere, and the authors listed in the submission have agreed on the content of this manuscript. Please feel free to contact me if you have any further queries regarding this submission.

Warmest regards,

Michele Rinaldi (et al.)

The importance of carbon to the formation and compositions of silicates during mantle metasomatism

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ABSTRACT

Mineral and fluid inclusions in mantle diamonds provide otherwise inaccessible information concerning the nature of mantle metasomatism and the role of fluids in the mass transfer of material through the Earth's interior. We explore the role of the carbon concentrations during fluid-rock metasomatism in generating the ranges of garnet and clinopyroxene compositions observed in diamonds from the sub-continental lithospheric mantle. We use the Deep Earth Water model to predict the results of metasomatism between silicic, carbonatitic and peridotitic fluids with common mantle rocks (peridotites, eclogites and pyroxenites) at 5 GPa, 1000 °C, across a range of redox conditions ($\log fO_2 = -2$ to $-4 \Delta FMQ$), and a wide range of initial carbon concentrations in the metasomatic fluids. Our results show that the predicted compositions of metasomatic garnets and clinopyroxenes are controlled by the initial compositions of the fluids and the rocks, with subsequent mineral-specific geochemical evolution following definable reaction pathways. Model carbon-rich, metasomatic fluids that can form diamond (initial C-content > 5.0 m) result in Mg-rich garnets and clinopyroxenes typical of peridotitic, eclogitic,

and websteritic inclusions in diamonds. However, model carbon-poor, metasomatic fluids that do not form diamond can result in Mg-poor, Ca-rich garnets and clinopyroxenes. Such garnets and clinopyroxenes can nevertheless occur as inclusions in diamonds. In our models, the abundance of carbon in the fluids controls the behaviour of the bivalent ions through the formation of aqueous Mg–Ca–Fe–C complexes which directly govern the composition of garnets and clinopyroxenes precipitated during the metasomatic processes. As the C-rich initial fluids can form the higher Mg-eclogitic, peridotitic, and websteritic inclusions in diamonds, these inclusions can be syngenetic (metasomatic) or possibly protogenetic. However, in our models, the relatively Mg-poor, Ca- and Fe-rich eclogitic garnet and clinopyroxene inclusions found in mantle diamonds formed from C-poor fluids that do not form diamonds. These inclusions most likely reflect a metasomatic event prior to being incorporated into their host diamonds, or they could represent a protolith-based protogenetic geochemistry.

Keywords: Diamond inclusions, fluid-rock metasomatism, thermodynamic modelling

1. INTRODUCTION

Experimental solubility data ([Manning, 2013](#); [Kessel et al. 2005a,b, 2015](#); [Förster et al., 2019](#)) and the cation concentration of fluid inclusions in diamonds ([Navon et al., 1988](#); [Weiss et al., 2015](#)) show that aqueous fluids in equilibrium with mantle rocks contain all the rock-forming major and trace elements required to precipitate mantle-forming silicates (olivine, pyroxene, garnet). Therefore, the interaction(s) between rocks, fluids, and melts is Earth's most efficient mechanism for the mass transfer of material throughout the solid Earth. However, direct samples are scarce, with rare melt inclusions in silicates and fluid inclusions in diamonds ([Weiss et al., 2022](#)) exceptions. Owing to their robust and inert nature, mantle diamonds are extraordinary archives which provide otherwise inaccessible samples of solids, liquids, and

gaseous material from Earth's mantle. Diamonds have formed over more than 75% of Earth's history (Gurney et al., 2010; Greß et al., 2020; Koornneef et al., 2017), with most forming in the sub-continental lithospheric mantle (120 – 180 km; Stachel and Harris, 2008; Stachel et al., 2022). Therefore, the geochemistry of diamond inclusions preserves the most detailed and intact history of mantle metasomatism.

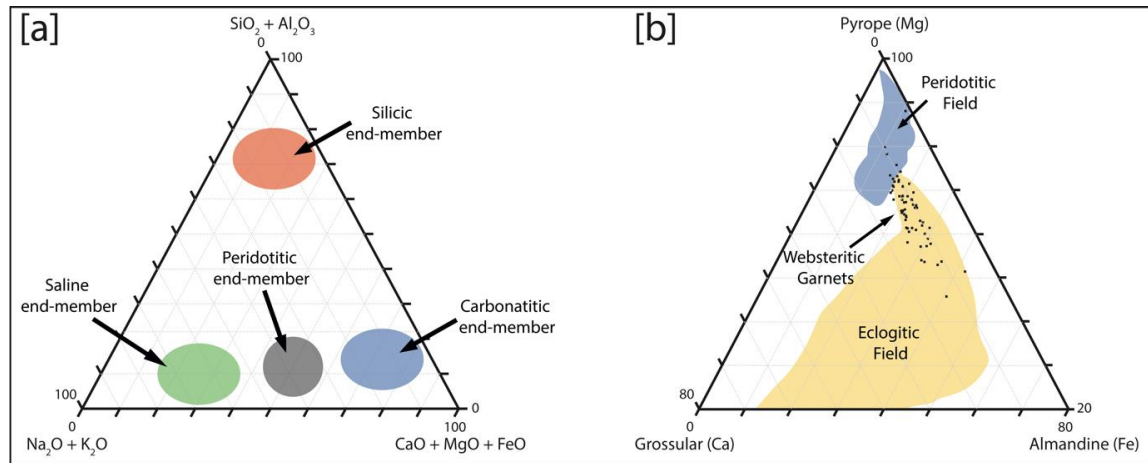


Figure 1. Fluid and solid inclusions in diamonds: a) End-member fluid inclusion compositions; (Weiss et al., 2022); b) Mineral inclusions from numerous sources (see Methods). Ternary compositions are plotted using the Python package python-ternary (Harper et al., 2019).

Diamonds are metasomatic precipitates (Shirey et al., 2013; Miller et al., 2014). Their crystallisation can be driven by the transport of carbon-bearing material across adiabatic, isobaric, and isothermal geochemical gradients (Palyanov et al., 2015; Jacob et al., 2014, 2016; Luth and Stachel, 2014; Stagno et al., 2015; Sverjensky and Huang, 2015; Mikhail et al., 2021). The geochemistry of fluid inclusions in diamonds reveals four end-member groups, termed silicic, peridotitic, carbonatitic and saline (Navon et al., 1988; Izraeli et al., 2001; Tomlinson et al., 2006; Weiss et al., 2009, 2014, 2022; Timmerman et al., 2021) (Fig.1a). The origin of diamond-forming fluids has been examined by experimental (e.g., Kessel et al., 2015; Meltzer and Kessel, 2022; Sonin et al., 2022; Förster et al., 2018; Bureau et al., 2018) and theoretical

approaches (Huang and Sverjensky, 2020; Mikhail et al., 2021), alongside studies predicting the geochemistry of diamond-forming fluids which would be in equilibrium with solid silicate inclusions (e.g., Mikhail et al., 2019; Stachel & Harris, 2008; Aulbach et al., 2009).

Compared with the geochemistry of the fluid inclusions in diamonds, the composition of the mineral inclusions is more diverse (e.g., garnets compositions in **Fig.1b**). Many mineral groups have been found as inclusions in diamonds, including sulfides, silicates, oxides, carbonates, and metallic phases (Stachel and Harris, 2008). However, one can subdivide these minerals into four groups peridotitic, eclogitic, websteritic, and exotic metallic phases (Stachel et al., 2022).

These classification schemes for both fluids and minerals are empirical; therefore, fluid and mineral classifications do not diagnostically inform us about petrogenetic processes (Mikhail et al., 2021). In particular, the diversity of the petrological characteristics and the complexity of structural and textural elements leave the interpretation of the genetic relationships between diamonds and their mineral inclusions unclear. The mineral inclusions can either reflect a pre-metasomatic heterogeneity in the host rock in the upper mantle (Pasqualetto et al., 2022), or they are the result of metasomatism coeval with diamond formation (Aulbach et al., 2002; Kiseeva et al., 2016; Mikhail et al., 2019a), or both options. Therefore, diamonds and their mineral inclusions can be either syngenetic (Harris, 1968; Mikhail et al., 2019a) or protogenetic (Nestola et al., 2017).

This contribution aims to investigate the geochemistry of silicates formed during isobaric (5 GPa) and isothermal (1000 °C) fluid-rock metasomatism benchmarked to the geochemistry of diamond inclusions. Specifically, we focused on garnets and clinopyroxenes because both are present in significant abundances in peridotitic, eclogitic, and websteritic paragenetic groups.

2. METHOD

Conceptually, our computational thermodynamic model involves two steps. Firstly, a fluid is equilibrated with a rock, this fluid then migrates and interacts with a collection of mineral phases (a rock) at the same (fixed) pressure and temperature (**Fig.2**). The fluid in step 2 is out of equilibrium with the rock, and this drives irreversible chemical reactions which produce new mineral phases while concurrent changes to the geochemistry of the fluid are reciprocated (e.g., [Huang and Sverjensky, 2020](#); [Mikhail et al., 2021](#)).

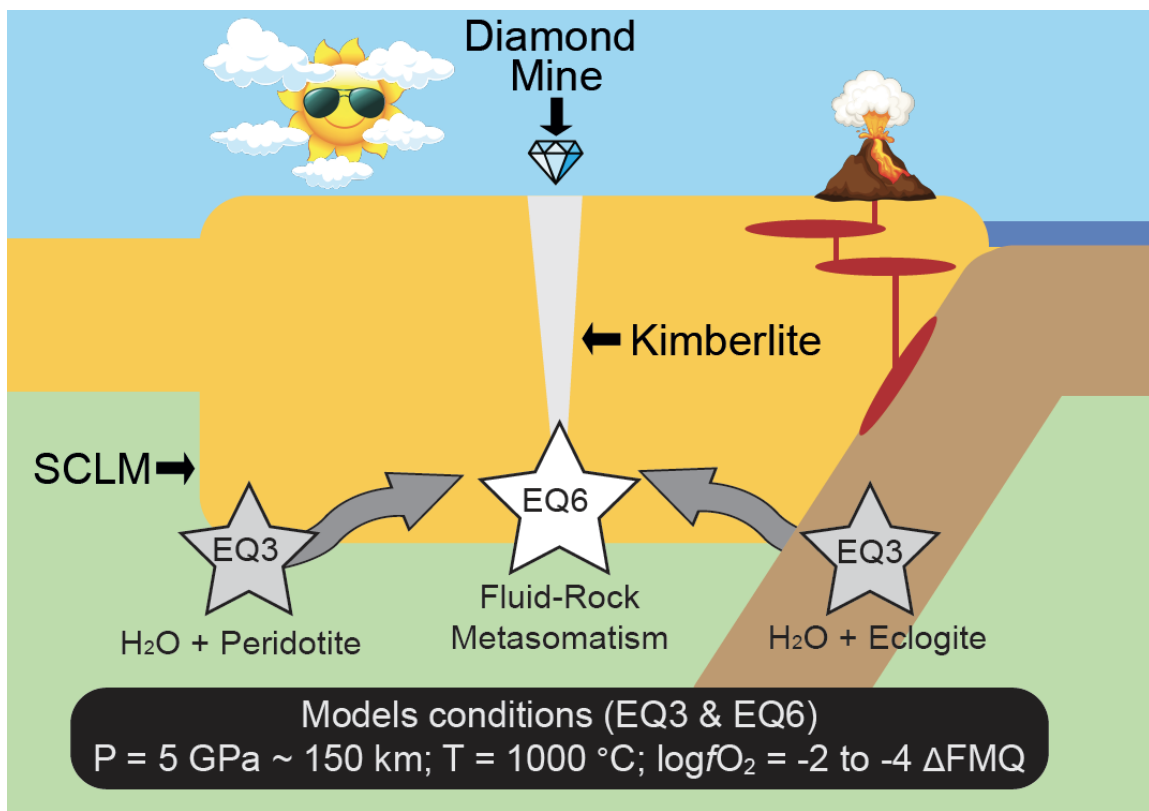


Figure 2 – Cartoon illustrating our conceptual modelling approach. We calculate the fluid composition for a given rock in equilibrium with water (EQ3), and then we compute the reaction of the resulting fluid with different lithologies (EQ6). Note that there are no spatial dimensions to our models. The fluid migration arrows shown above illustrate – contextually – the formation and migration of a mantle fluid which migrates into the cratonic lithosphere and reacts with rocks that it encounters (i.e., fluid metasomatism in the SCLM).

107

108 The range of initial carbon contents of the fluids used in the modelling can be related to
109 different geological contexts, from the breakdown of hydrous wadsleyite into olivine + H₂O
110 during a rising of a plume in the subcontinental lithosphere (low carbon fluids) to a fluid
111 migrating from sediments carried downwards by the slab in a subduction zone (high carbon
112 fluids; [Poli et al., 2015](#); [Tumiati et al., 2017](#); [Yaxley et al., 2021](#)). The P-T-X conditions we
113 used (P = 5 GPa, T = 1000 °C, $fO_2 = \Delta FMQ -2$ to -4) overlap with the average P-T-X conditions
114 for lithospheric diamond inclusion formation where the average inclusion entrapment
115 temperature is 1155 ± 105 °C (n = 444) and pressure is 5.3 ± 0.8 GPa (n = 157) ([Stachel and](#)
116 [Harris, 2008](#); [Stachel and Luth, 2015](#)).

117 Fluid-rock interaction is complex and dynamic, where solid and fluid phases interact
118 progressively. This results in irreversible geochemical evolution. Thermodynamic modelling
119 of fluid-rock interaction above 0.5 GPa was precluded until the dielectric constant of water was
120 constrained at ≤ 6 GPa ([Sverjensky et al., 2014](#)). Now, we can apply the Helgeson-Kirkham-
121 Flowers (HKF) equations of state for aqueous speciation ([Helgeson and Kirkham, 1974a,b,](#)
122 [1976](#); [Helgeson et al., 1981](#); [Tanger and Helgeson, 1988](#); [Shock and Helgeson, 1988](#);
123 [Sverjensky et al., 1997](#)) up to 6 GPa and 1200 °C ([Pan et al., 2013](#); [Facq et al., 2014](#); [Sverjensky](#)
124 [et al., 2014](#)). As a result, it is now possible to model the fluid speciation of aqueous anions,
125 metal complexes, and neutral species and their interaction with minerals across pressure and
126 temperature conditions that resemble those from the surface and down to ca. 150 km inside
127 planet Earth ([Huang and Sverjensky, 2019, 2020](#); [Mikhail et al., 2021](#)).

128 The initial fluid compositions we used are designed to mirror endmember compositions of fluid
129 inclusions from diamonds described in the literature (i.e., silicic, peridotitic and carbonatitic;
130 [Weiss et al., 2009](#), [Weiss et al., 2022](#); **Fig.1a**), which are equilibrated with a specific mantle
131 rock (e.g., mineral assemblage; **Table 1**, **Table S1-S3**). The silicic fluid is based on an

experimental calibration of aqueous fluid in equilibrium with a mafic eclogite (Kessel et al., 2015; later referred to as an eclogitic fluid), documented in Huang and Sverjensky (2020). For the peridotitic and carbonatitic fluids, we chose the peridotite and carbonated dunite used to model the fluid endmembers to form Panda diamonds (Huang and Sverjensky, 2020), with garnet instead of spinel to match the higher temperature and pressure. We assumed ideal site-mixing of garnet endmembers (pyrope, grossular and almandine) and a non-ideal mixing of clinopyroxene endmembers (diopside, clinoenstatite and hedenbergite) as used in previous work (Huang and Sverjensky, 2020; Mikhail et al., 2021). To study the influence of carbon abundance and speciation on the geochemistry of silicate minerals, we ran models with variable initial amounts of carbon (from 0 to 8.5 molal; **Table S3**) for the eclogitic and peridotitic fluids. Due to the nature of the carbonatitic fluid, it was impossible to constrain the amount of carbon with a fixed value as it would have affected the entire mineral assemblage (e.g., carbonates). Therefore, carbon was set in equilibrium with diamond for the carbonatitic fluid, and the model calculated the most stable mineral assemblage in the system. Finally, to allow the like-for-like comparison with the carbonatitic fluid, we also simulated a suite of peridotitic and eclogitic fluid-rock reactions in equilibrium with diamond (labelled as Type: Diamond in **Table 1** and **Table S2**).

Fluid	Type	Name	C	K	Na	Ca	Mg	Fe	Al	Si	Cl	pH
Eclogitic	Low-C fluids	E_0.0	0	0	1.05	0.68	0.013	0.057	1.16	11.57	0	4.49
		E_0.25	0.25	0	1.05	0.69	0.053	0.073	1.19	11.52	0	4.51
		E_0.50	0.5	0	1.04	0.7	0.09	0.087	1.21	11.46	0	4.52
		E_0.75	0.75	0	1.04	0.72	0.13	0.1	1.23	11.41	0	4.53
		E_1.0	1	0	1.04	0.73	0.16	0.12	1.25	11.36	0	4.54
	Diamond	E_dia	3.13	0	1.05	0.84	0.42	0.22	1.37	10.91	0	4.6
Peridotitic	Low-C fluids	P_0.0	0	2.45	2	0.78	0.21	1.71	0.1	2.36	8	4.51
		P_0.25	0.25	2.41	2	0.78	0.33	1.69	0.1	2.46	8	4.53
		P_0.50	0.5	2.37	2	0.79	0.46	1.67	0.1	2.56	8	4.54
		P_0.75	0.75	2.34	2	0.8	0.58	1.65	0.1	2.66	8	4.55
		P_1.0	1	2.3	2	0.81	0.7	1.63	0.11	2.78	8	4.56
	Diamond	P_dia	5.58	1.91	2	1.03	2.48	1.36	0.14	4.25	8	4.73
Carbonatitic	Diamond	C_dia	17.96	0.5	0.5	11.13	3.01	0.68	0.72	0.08	1	5.8

Table 1 – Composition of eclogitic, peridotitic, and carbonatitic fluids at 1000 °C, 5 GPa and $\Delta\text{FMQ} -3$.

151

152 The mineralogy (geochemistry) of the reactant (rocks) are benchmarked to nature using
 153 empirical data from natural samples: peridotites (Pearson et al., 2014), eclogites (Pearson et
 154 al., 2014; Sverjensky et al., 2015) and pyroxenites (Gonzaga et al., 2010; Farré-de-Pablo et al.,
 155 2020; Liu et al., 2022; Lu et al., 2022). Three lithologies represent each rock family with
 156 different mineral abundances and solid solution compositions (Table 2). The decision to
 157 include pyroxenites was taken due to the predicted relationship between diamonds and
 158 pyroxenites, as suggested by Kiseeva et al. (2016).

159 The model outputs a large amount of data (Supplementary File, Table S4-S6). The chemistry
 160 of fluids and metasomatic minerals is relevant for this study at each reaction stage until the
 161 system is fully equilibrated. Reaction progress is quantified using the reaction variable ξ , which
 162 expresses the destruction of 1.0 mole of each reactant mineral per 1.0 kg of H₂O in the initial
 163 fluid. To compare with natural data, we plotted the model results over a database of lithospheric
 164 diamond inclusion geochemistry, including the major element data for olivine (n = 1334),
 165 orthopyroxene (n = 446), clinopyroxene (n = 926) and garnet (n = 2628) (Stachel and Harris,
 166 2008; Gurney and Boyd, 1982; Gurney et al., 1984; Viljoen et al., 1999; Jacob et al., 2000;
 167 Tappert et al., 2005; De Stefano et al., 2009; Sobolev et al., 2009; Tappert et al., 2009;
 168 Bulanova et al., 2010; Dobosi and Kurat, 2010; Miller et al., 2014; Mikhail et al., 2019). All
 169 input and output files are available at <https://doi.org/10.17630/9573e741-2787-4d70-b47a-60e567abccf7>.
 170

Rock	Mineral composition (% in volume)
Lherzolite	55% ol (Fo _{0.930}), 20% opx (En _{0.938} Fe _{0.062}), 20% cpx (Di _{0.294} Hdn _{0.088} Ja _{0.014} En _{0.603}), 5% grt (Py _{0.733} Gr _{0.137} Alm _{0.130})
Harzburgite	71% ol (Fo _{0.933}), 24% opx (En _{0.938} Fe _{0.062}), 5% grt (Py _{0.733} Gr _{0.137} Alm _{0.130})
Dunite	85% ol (Fo _{0.930}), 5% opx (En _{0.938} Fe _{0.062}), 5% cpx (Di _{0.294} Hdn _{0.088} Ja _{0.014} En _{0.603}), 5% grt (Py _{0.733} Gr _{0.137} Alm _{0.130})
Eclogite type 1	42% cpx (Di _{0.200} Hdn _{0.100} Ja _{0.700} En _{0.000}), 26% grt (Py _{0.600} Gr _{0.100} Alm _{0.300}), 32% coe

Eclogite type 2	25% cpx ($\text{Di}_{0.200}\text{Hdn}_{0.100}\text{Ja}_{0.700}\text{En}_{0.000}$), 50% grt ($\text{Py}_{0.333}\text{Gr}_{0.334}\text{Alm}_{0.333}$), 25% coe
Eclogite type 3	25% cpx ($\text{Di}_{0.200}\text{Hdn}_{0.100}\text{Ja}_{0.700}\text{En}_{0.000}$), 75% grt ($\text{Py}_{0.200}\text{Gr}_{0.600}\text{Alm}_{0.200}$)
Websterite	5% ol ($\text{Fo}_{0.920}$), 45% opx ($\text{En}_{0.750}\text{Fe}_{0.250}$), 45% cpx ($\text{Di}_{0.560}\text{Hdn}_{0.020}\text{Ja}_{0.020}\text{En}_{0.400}$), 5% grt ($\text{Py}_{0.500}\text{Gr}_{0.250}\text{Alm}_{0.250}$)
Orthopyroxenite	5% ol ($\text{Fo}_{0.890}$), 90% opx ($\text{En}_{0.900}\text{Fe}_{0.100}$), 5% grt ($\text{Py}_{0.700}\text{Gr}_{0.100}\text{Alm}_{0.200}$)
Clinopyroxenite	5% ol ($\text{Fo}_{0.930}$), 90% cpx ($\text{Di}_{0.700}\text{Hdn}_{0.025}\text{Ja}_{0.250}\text{En}_{0.025}$), 5% grt ($\text{Py}_{0.250}\text{Gr}_{0.500}\text{Alm}_{0.250}$)

Table 2 – Mineralogical and solid solution compositions of mantle rocks used during fluid-rock interaction.

3. RESULTS

The results of the model runs are given in Supplementary files, **Table S4-S6**. This study focuses on the composition of the fluid and solid components, including the solid solution geochemistry of each applicable phase and the speciation of aqueous components dissolved in the fluid as a function of reaction progress (ξ). The metasomatic minerals formed during the reaction are silicates (olivine, pyroxenes, and garnet), oxides (magnetite, hematite and meionite), carbonates (dolomite), and native phases (diamond) (**Table S4**). Except for minor meionite, the mineral phases precipitated in our models are consistent with those found as inclusions in mantle diamonds (Stachel et al., 2022). Meionite is formed because the system needs to compensate for the high activities of calcium and carbon in the early stages of the fluid-rock interaction under conditions where carbonates and clinopyroxenes are not stable. As the reaction progresses, meionite is mainly supplanted by silicate minerals, carbon-rich aqueous species, and occasionally, diamond. Our models show that the precipitation of metasomatic garnets and clinopyroxene with a chemical composition covering almost entirely the range of silicate minerals found as inclusions in diamonds is possible during fluid metasomatism of the SCLM. Garnet and clinopyroxene are present in the final stages of every model presented in this work, along with orthopyroxene and, sometimes, olivine (**Table S4**). Herein, we focus on

the chemical evolution of garnets and clinopyroxene because these phases are present and common in all three paragenetic diamond inclusion groups.

3.1 – Reaction products as a function of fluid type (diamond-forming fluids)

Selected models charting the geochemical evolution of precipitated garnets and clinopyroxenes are shown in **Fig. 3a-f**. These data show, as can be expected, that those reactions with the most significant chemical disequilibrium between fluid and rock produce the broadest compositional range of silicate precipitates. For example, model runs for an eclogitic fluid reacting with a lherzolite (**Fig. 3c-d**) show a wide variation in garnet and clinopyroxene compositions.

Consistent with the findings for eclogitic fluid-rock metasomatism reported previously ([Mikhail et al., 2021](#)), varying the silicate mineral abundances and solid-solution compositions in the host rock does not strongly influence the geochemistry of the precipitates from a given fluid.

We find the composition of garnets precipitated from both the eclogitic and peridotitic fluids reacting with all mantle lithologies overlaps with natural diamond inclusion data on the pyrope-grossular-almandine ternary with garnet compositions transecting the fields encompassing high-Mg eclogitic, websteritic, and peridotitic garnet inclusion compositions (**Figs. 3a and 3c**).

The composition of clinopyroxenes precipitated from the peridotitic fluid shows Mg-enrichment and Fe-depletion outside the range observed in the natural diamond inclusion dataset (**Fig. 3b**). In contrast, the composition of clinopyroxenes precipitated from the eclogitic fluid shows substantial overlap with the natural diamond inclusion dataset in wollastonite-enstatite-ferrosilite space, crossing the field for eclogitic, websteritic, and peridotitic compositions (**Fig. 3d**).

For the carbonatitic fluid, we find that the garnets produced have hereto unseen, very high, grossular contents because of the elevated Ca-content (dissolved Ca-carbonate) in the system

216 **(Fig. 3e)** and produce clinopyroxenes with appropriate Ca-Mg ratios and severely depleted Fe
 217 contents **(Fig. 3f)**. Therefore, we do not consider models involving this carbonatitic fluid
 218 furthermore. Still, we provide ternary diagrams showing the results for carbonatitic fluid
 219 models in the Supplementary file **(Fig. S1)**.

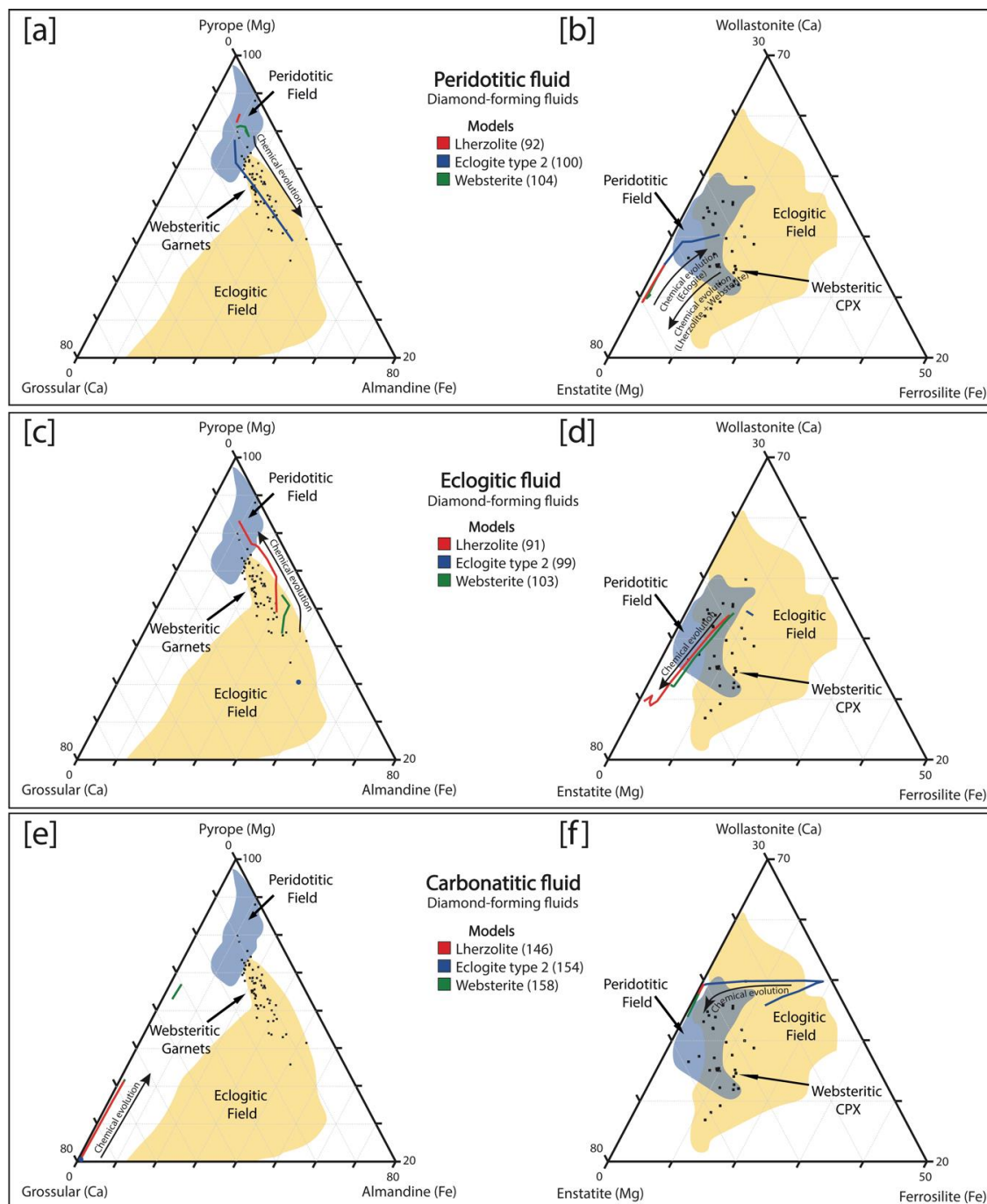


Figure 3 – The geochemistry of garnets and clinopyroxenes precipitated during progressive fluid-rock interaction for peridotitic (a, b), eclogitic (c, d) and carbonatitic (e, f) diamond-forming fluids with a range of host rocks (lherzolite, eclogite type 2, and websterite) at 1000 °C, 5 GPa and -3 ΔFMQ. The initial amount of carbon in the fluids is determined by equilibrium with diamond (diamond-forming fluids) and varies from about 3 to 18 molal.

3.2 – Reaction products as a function of the carbon content of the fluid

The trends described above for the model predicted garnet and clinopyroxene compositions consistent with carbon-rich initial fluids (i.e., diamond-forming fluids) serve as reference trends described by the black lines in **Figs. 4a - d**. Among the most abundant dissolved carbon species in these fluids are species such as $\text{Ca}(\text{HCOO})^+$, $\text{Fe}(\text{HCOO})^+$ and $\text{Mg}(\text{SiO}_2)(\text{HCO}_3)^+$ (**Table S3 and Table S6**). Therefore, a rational assumption would be that aqueous Mg–Ca–Fe–C complexes will exert control on the behaviour of Mg^{2+} , Ca^{2+} and Fe^{2+} , which would be reflected in the composition of calcium-bearing ferromagnesian silicates. Indeed, we find that the carbon content of the fluid does greatly influences the chemical composition of garnets and clinopyroxenes precipitated during fluid-rock interaction. In short, the lower the carbon content in the fluid, the lower the Mg-contents in garnet and clinopyroxene precipitates (**Figs. 4a -d**). For example, it can be seen in **Figs. 4a and c** that model carbon-poor fluids (less than or equal to 1.0 m) show a very different chemical evolution to the carbon-rich, diamond-forming fluid in terms of the predicted compositions of garnets. In fact, the lowest carbon fluids (C-free) are consistent with garnets with pyrope contents of only 30% (**Figs. 4a and 4c**). The same fluids are consistent with clinopyroxenes with enstatite contents as low as about 50%, and high wollastonite and ferrosilite contents (**Figs. 4b and 4d**). The range of predicted model clinopyroxene compositions results in model trajectories which cross from the truly eclogitic

(Fe-rich + Mg-poor) areas of these ternary diagrams into the Mg-rich and definitively peridotitic domain(s) (**Figs. 4b and d**).

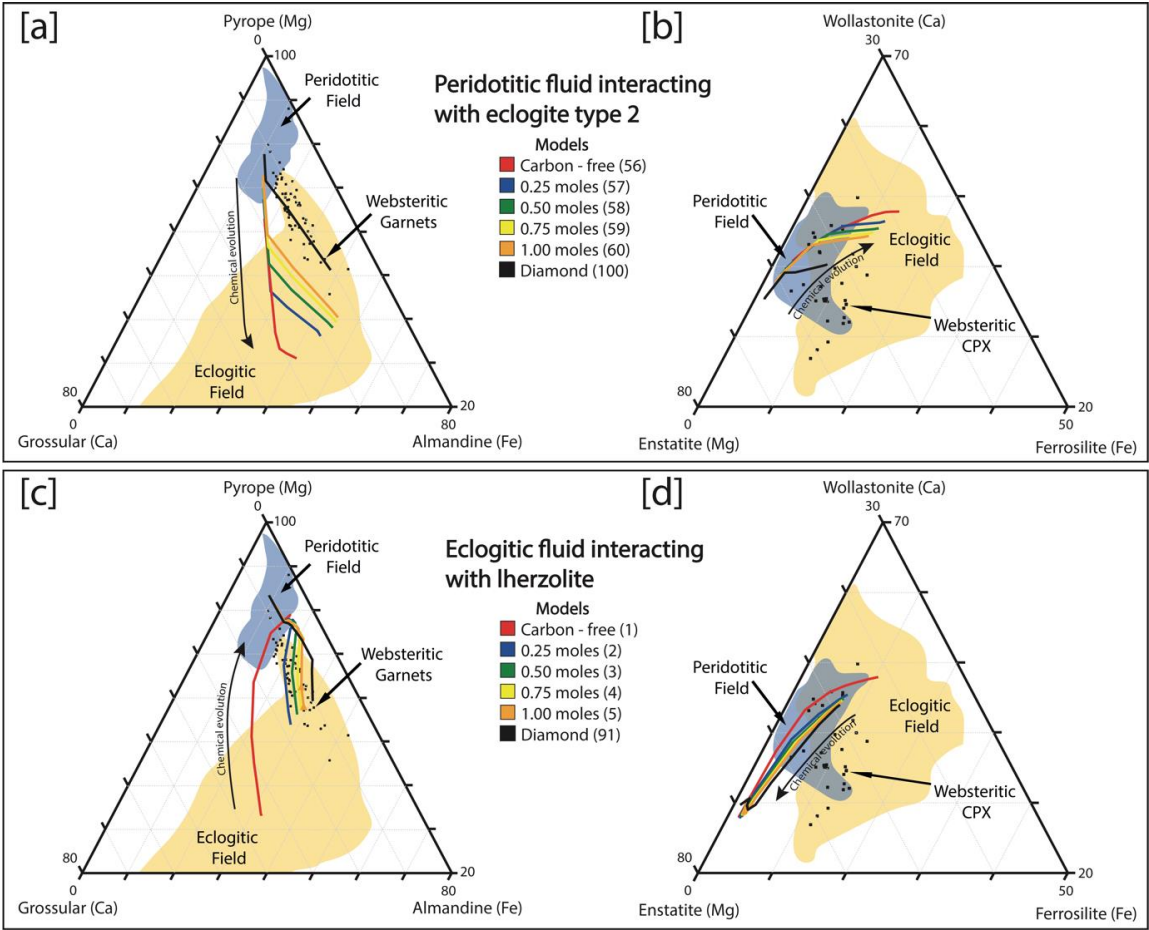


Figure 4 – Results for models with variable carbon contents. Garnets and clinopyroxene chemical composition resulting from the interaction between a peridotitic (a, b) and eclogitic (c, d) fluids with a range of host rocks (lherzolite, eclogite type 2, and websterite) at 1000 °C, 5 GPa and -3 Δ FMQ. The amount of carbon varies from carbon-free to those in equilibrium with diamond.

4. DISCUSSION

4.1 – Chemical evolution during carbon-bearing fluid-rock interaction

The systems investigated in this study are isobaric and isothermal, where each run has a fixed starting fO_2 . We observe minor (and trivial) variations in oxygen fugacity (in the second decimal place) and pH during each run. Consequently, the driving force for metasomatism is the chemical gradient established between the system's two components, a model rock and a model fluid. Our models predict that fluid-rock interaction will result in progressive silicate formation with evolving major element compositions. Both fluids and rocks play a role in mineral evolution. Counter-intuitively, host rock mineralogy is not always reflected in the geochemistry of the precipitates at each reaction stage. Instead, the geochemistry of the fluid dominates the nature of mineral precipitates in the early stages (low ξ). However, the mineral composition of the precipitates eventually converges with those of the host rock at high ξ . For example, the first garnets and pyroxenes precipitating from an eclogitic fluid reacting with a lherzolite are grossular- and diopside-rich, but the final garnets precipitating at the end of the same reaction pathway are relatively pyrope- and enstatite-rich (**Figs. 3c-d and 4c-d**). Additionally, the clinopyroxenes formed by a peridotitic fluid reaction with a lherzolite and websterite increase its enstatite component when the host rock is more Mg-rich than the peridotite which formed the peridotitic fluid (**Fig. 3a**).

We use data from lithospheric diamond inclusions as a calibrant for model accuracy. For garnets, both carbon-poor eclogitic and peridotitic fluids precipitate garnets that transect (peridotitic fluid; **Fig. 4a**) or straddle the spread of natural data (eclogitic fluid; **Fig. 4c**). These carbon-poor fluids do not produce diamond in our models. In contrast, the carbon-rich, diamond-forming fluids in our model produce garnet with >50% pyrope. These constraints prevent the prediction of the formation of pyrope-poor eclogitic garnets together with diamond during the same metasomatic events. However, the majority of eclogitic garnet inclusions in diamonds are pyrope-poor (**Fig. 1b**). For clinopyroxenes, the models with peridotitic fluids precipitate sub-calcic clinopyroxenes (<35% Wo) with meagre ferrosilite contents meaning

that – save for the latest-stage precipitates – none resemble clinopyroxenes from the lithospheric diamond inclusion database (**Fig. 4b**). However, a better fit is found for eclogitic fluids reacting with websterites and peridotites (**Fig. 4d**).

Whilst far from encompassing the range of garnet and clinopyroxene major element compositions found in lithospheric diamonds, these models corroborate the notion that eclogitic, websteritic, and peridotitic garnets and clinopyroxene inclusions in lithospheric mantle diamonds can be genetically related to one another by a single metasomatic event ([Mikhail et al., 2021](#)). We show that this notion holds, non-exclusively, for metasomatic garnets and clinopyroxenes precipitated during eclogitic- and peridotitic-fluid metasomatism with host all main mantle-forming host rock types (peridotite, websterite, and eclogite).

4.2 – Chemical evolution during carbon-poor fluid-rock interaction

Any individual diamond-hosted mineral inclusion is either syngenetic ([Harris, 1968](#); [Mikhail et al., 2019a](#)) or protogenetic ([Pasqualetto et al., 2022](#); [Nestola et al., 2017](#)) to the host diamond. If syngenetic, the formation of the inclusion in a diamond is the result of carbon-rich fluid metasomatism, according to our models. Our data imply that diamond-forming fluids cannot produce pyrope-poor garnets and wollastonite + ferrosillite-rich clinopyroxenes under the conditions employed in this study. This may suggest that pyrope-poor garnet and wollastonite + ferrosillite-rich clinopyroxene inclusions are protogenetic, and their geochemistry should reflect their protolith (eclogite). Alternatively, they may reflect a previous metasomatic event before being incorporated into diamond. In both cases, the inclusions can be thought of as protogenetic, and these samples would be incredibly valuable tracers of metasomatism, mantle melting, and subduction events through deep time. Our models predict that the amount of carbon strongly influences garnet and clinopyroxene major element compositions precipitated from the fluid. As indicated above, most carbon-poor

fluids form Mg-poor and Ca-rich garnets (**Figs. 4a and 4c**) and clinopyroxene (**Figs. 4b and 4d**). Metasomatic reactions for both carbon-poor peridotitic fluids (**Fig. 4a and 4b**) and carbon-poor eclogitic fluids (**Fig. 4c and 4d**) result in the precipitation of garnets and clinopyroxenes deep in the eclogitic field of data, where Ca-rich phases dominate. In contrast, carbon-rich fluid initially in equilibrium with diamond resulted in Mg-rich garnets (**Figs. 3a and 3c**) and clinopyroxene (**Figs. 3b and 3d**), covering the whole range of peridotitic and websteritic inclusions but barely entering the low-Mg eclogitic field.

As anticipated, we attribute the effects of variable carbon concentration on the silicate product minerals to the speciation of bivalent ions as Mg–Ca–Fe–C aqueous complexes during the metasomatic process. The model Mg-rich aqueous species are more abundant in the more-oxidized carbon-rich systems, consistent with experimental data ([Tiraboschi et al., 2018](#)). Evidence for the role of oxygen fugacity on the aqueous speciation is found by examining the effect of different oxygen fugacities ($fO_2 = -2$ to -4 ΔFMQ) on the composition of silicate precipitates during the fluid-rock interaction (**Fig. S2**). The amount of carbon in the fluid and its speciation are susceptible to variations in the redox conditions (**Table 1, Table S2-S3**). By lowering the oxygen fugacity, the total Mg/total C ratio decreases because of the differences in the Mg-silicate-bicarbonate and Ca-formate aqueous complexes. This means a proportional higher availability of Ca-formate complexes, leading to the formation of Ca-rich silicates, which cross deeper into the eclogitic field.

4.3 – Implications for diamond-inclusion petrogenesis

Carbon speciation does not solely control silicate composition, it is also linked to the formation of diamond. However, diamond is not formed in the carbon-poor models in this study (**Table S4**). Because the Mg-poor minerals are predicted to require low-carbon fluids to form during fluid-rock metasomatism, our data imply that Mg-poor eclogitic inclusions in diamonds did not

form during the metasomatic event that also formed their host diamonds. The inclusions are therefore likely protogenetic. Their geochemistry should strongly reflect an eclogite protolith or, alternatively, a metasomatic event prior to the formation of the host diamond. Conversely, our data suggest that model, carbon-rich, metasomatic fluids that can form diamond result in Mg-rich garnets and clinopyroxenes during metasomatism of common mantle rocks. This result implies that peridotitic and websteritic garnets and clinopyroxenes can be either syngenetic or protogenetic.

5. CONCLUSIONS

We modelled the interaction between three fluid endmembers found in fluid inclusions in diamonds (peridotitic, eclogitic and carbonatitic) with a broad range of mantle rocks (peridotites, eclogites and pyroxenites) at conditions relevant for diamond formation (1000°C, 5 GPa, -2 to -4 Δ FMQ) to simulate fluid-rock metasomatism. We specifically focused on a wide range of initial carbon concentrations in the metasomatic fluids to explore the effects on the chemical evolution of garnets and clinopyroxenes during metasomatic processes. We studied how different fluids, rocks, amounts of carbon, and environmental conditions can influence the major element compositions of silicate inclusions in diamonds.

Our results show that the driving force for silicate evolution is the chemical gradient established between the host rock and the fluid, leading to the possibility of connecting different paragenetic groups along a single reaction pathway in an isobaric and isothermal system. Both fluids and host rocks play an important role in controlling the silicate chemical evolution: the fluid is responsible for the initial composition of metasomatic minerals, and later, when the magnitude of fluid-rock interaction increases, the host rock becomes dominant. These data highlight how paragenetic groups of inclusions from diamonds are not necessarily directly related to a particular geological environment in every case. Instead, the traditional paragenetic

groups can reflect the extent of the metasomatic process and the nature of the original metasomatic fluid.

Importantly, the amount of carbon in the initial fluid strongly influences the compositions of the silicate minerals formed during metasomatism. Carbon-poor fluids are necessary to form Mg-poor, Ca-rich garnets and clinopyroxenes, but do not form diamond under the conditions we examined. This result suggests that a syngenetic origin of diamonds and low-Mg eclogitic inclusions may not be feasible during the same metasomatic event. Such inclusions in diamonds may well be protogenetic. In contrast, carbon-rich fluids can precipitate Mg-rich minerals and diamond. Therefore, peridotitic and websteritic inclusions in diamonds can be either syngenetic or protogenetic, and no single notion can be championed beyond a reasonable doubt without direct evidence from the sample(s) in question (e.g., possibly via crystallographic orientation relationships, relative geochronology, major element geochemistry of multiple inclusions in a single diamond, trace element or noble gas systematics of diamond + inclusion).

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APPENDIX A. SUPPLEMENTARY MATERIAL

The Supplementary Material contains the composition and carbon speciation of the fluids before and after the fluid-rock interaction, and the final rock composition for the most relevant models. Ternary plots for different rocks and variations in oxygen fugacity are also available.

RESEARCH DATA

Research Data associated with this article can be accessed at <https://doi.org/10.17630/9573e741-2787-4d70-b47a-60e567abccf7>. The dataset is hosted by PURE (St Andrews University repository system).

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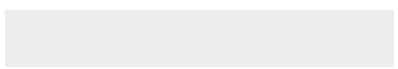
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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