Carbon isotope fractionation during diamond growth in depleted peridotite: Counterintuitive insights from modelling water-maximum CHO fluids as multi-component systems

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ABSTRACT

Because of the inability of depleted cratonic peridotites to effectively buffer oxygen fugacities when infiltrated by CHO or carbonatitic fluids, it has been proposed recently (Luth and Stachel, 2014) that diamond formation in peridotites typically does not occur by rock-buffered redox reactions as previously thought but by an oxygen-conserving reaction in which minor coexisting CH_4 and CO_2 components in a water-rich fluid react to form diamond ($CO_2 + CH_4 = 2C + 2H_2O$). In such fluid-buffered systems, carbon isotope fractionation during diamond precipitation occurs in the presence of two dominant fluid carbon species. Carbon isotope modelling of diamond precipitation from mixed CH_4- and CO_2-bearing fluids reveals unexpected fundamental differences relative to diamond crystallization from a single carbon fluid species: (1) irrespective of which carbon fluid species (CH_4 or CO_2) is dominant in the initial fluid, diamond formation is invariably associated with progressive minor ($<1‰$) enrichment of diamond in ^{13}C as crystallization proceeds. This is in contrast to diamond precipitation by rock-buffered redox processes from a fluid containing only a single carbon species, which can result in either progressive ^{13}C enrichment (CO_2 or carbonate fluids) or ^{13}C depletion (CH_4 fluids) in the diamond. (2) Fluid speciation is the key factor controlling diamond $\delta^{13}C$ values; as X_{CO_2} ($X_{CO_2} = CO_2/[CO_2 + CH_4]$) in the initial fluid increases from 0.1 to 0.9 (corresponding to an increase in fO_2 of 0.8 log units), the carbon isotope composition of the first-precipitated diamond decreases by 3.7‰. The tight mode in $\delta^{13}C$ of $-5 \pm 1‰$ for diamonds worldwide places strict constraints on the dominant range of X_{CO_2} in water-rich fluids responsible for diamond formation. Specifically, precipitation of diamonds with $\delta^{13}C$ values in the range -4 to $-6‰$ from mantle-derived fluids with an average $\delta^{13}C$ value of $-5‰$ (derived from evidence not related to diamonds) requires that diamond-forming fluids were relatively reduced and had methane as the dominant carbon species ($X_{CO_2} = 0.1$–0.5).

Application of our model to a recently published set of in-situ carbon isotope analyses for peridotitic diamonds from Marange, Zimbabwe (Smit et al., 2016), which contain CH_4 fluid inclusions, allows us to perfectly match the observed co-variations in $\delta^{13}C$, $\delta^{15}N$ and N content and at the same time explain the previously counter-intuitive observation of progressive ^{13}C enrichment in diamonds that appear to have grown from a fluid with methane as the dominant carbon species. Similarly, the almost complete absence in the published record of progressive ^{13}C depletion trends within diamonds likely reflects ubiquitous precipitation from CH_4- and CO_2-bearing water-rich fluids, rather than diamond formation exclusively by carbonate-bearing and CH_4-free oxidized fluids or melts.

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1. Introduction

Diamond is a metasomatic mineral introduced into mantle rocks through percolating carbon-bearing fluids or melts (Haggerty, 1986; Stachel and Harris, 1997; Taylor et al., 1998). The lithospheric mantle beneath Archean cratons is the principal source of kimberlite- and lamproite-borne diamonds and depleted peri- dotite (harzburgite) is the dominant substrate for diamond forma- tion (Gurney, 1984; Boyd and Gurney, 1986; Stachel and Harris, 2008). From the high solidus temperature of harzburgite, even in the presence of carbonate and water, it can be concluded that di- amonds in harzburgitic substrates must have precipitated under sub-solidus conditions from CHO fluids (Boyd and Gurney, 1986; Stachel and Harris, 1997; Stachel and Luth, 2015).

The widely accepted model of diamond formation involves redox reactions between such percolating CHO fluids (or under

supra-solidus conditions, low volume melts) and their wall rocks. This redox-based model has been challenged recently by Sverjensky and coworkers, who argue for diamond formation as a result of changes in pH during fluid reaction with coesite- and kyanite-bearing eclogite at 900 °C and 5 GPa (Sverjensky and Huang, 2015) by reactions such as $CH_3CH_2COO^- + H^+ = 3C + H_2 + 2H_2O$ (Sverjensky and Huang, 2015) or $CH_3COO^- + H^+ = 2C + 2H_2O$ (Sverjensky et al., 2014). In the latter paper, they calculated that the fluid in equilibrium with peridotite along a cratonic geotherm, in contrast, would "consist of the traditional COH fluid species" (i.e., CO_2, CH_4, and CO, as shown in their Fig. 4b), rather than any ionic species. Given that our discussion focuses on diamond formation in harzburgites, our treatment of the fluid as neutral species is consistent with their calculations.

In the redox-based model, diamond-forming reactions involve either carbonate (or CO_2) reduction (Rosenhauer et al., 1977; Eggler and Baker, 1982) or CH_4 oxidation (Taylor and Green, 1989), depending on the relative redox states of the fluid and wall rock. The question of which of the two proposed redox reactions is responsible for the formation of a particular population of diamonds or which dominates globally is of great interest and, in principle, can be addressed solely through stable isotope analyses of diamond: in systems where oxygen fugacity is controlled by the host rocks, diamond precipitation from reducing (CH_4 as the dominant carbon species) and oxidizing (CO_2 or CO_3^{2-} as the dominant carbon species) fluids or melts produces opposite evolutionary trends in the carbon isotope composition of diamonds, which may be tracked by examining population frequency distributions (Deines, 1980; Stachel and Harris, 2009) or core to rim C-isotope variations of single crystals (Zedgenizov et al., 2006; Smart et al., 2011). Of these two approaches to tracking evolutionary trends during diamond formation, the examination of isotopic zoning profiles in continuous growth zones in individual diamonds is clearly more robust for assessing diamond-forming processes as the shape of frequency distributions for entire diamond populations may merely reflect the sum of multiple diamond growth events from distinct fluids (different initial isotopic composition and redox state) that may have occurred over large time spans.

The assumption underpinning the model of redox-driven diamond precipitation is that the fO_2 of the lithospheric mantle is buffered by ferrous–ferric iron equilibria in the constituent rocks. This keystone was, however, recently removed when Luth and Stachel (2014) showed that the buffering capacity of depleted cratonic peridotite (the main diamond substrate) is so low that the oxygen fugacity of lithospheric mantle is effectively fluid- rather than wall rock-buffered. In a fluid-buffered environment, direct crystallization of diamond (closed system) from cooling or ascending (simultaneous cooling and depressurization) fluids may provide alternative modes of diamond formation (Luth and Stachel, 2014; Stachel and Luth, 2015). Isochemical diamond precipitation is governed by two oxygen-conserving reactions:

$$CO_2 + CH_4 = 2C + 2H_2O \quad \text{(Deines, 1980)} \qquad (1)$$

$$2C_2H_6 = 3CH_4 + C \qquad (2)$$

with reaction (1) occurring during cooling (isobaric and/or during ascent along a geotherm) and (2) being driven by contraction of the ethane field with decreasing pressure. Reaction (2) involving ethane only becomes an important diamond-forming reaction in fairly reduced fluids (below $\Delta \log fO_2(FMQ) - 3$) and observations of the associated trend of progressive ^{13}C depletion are extremely rare (e.g., Thomassot et al., 2007); as such, reaction (1) is the primary focus of the present study.

The speciation of carbon-saturated CHO fluids percolating through the subcratonic lithospheric mantle is a function of pressure, temperature and an additional intensive variable. For situations in which the oxidation state is imposed on the fluid, the traditional choice for this variable is oxygen fugacity (fO_2) (Taylor and Green, 1989; Wood et al., 1990; Luth, 2003). In situations where the oxidation state is not imposed on the fluid by the surrounding rocks (e.g., percolation of fluid through depleted cratonic peridotites), a more appropriate choice would be a fluid compositional variable such as O/(O + H). The fO_2 conditions of typical cratonic mantle in the diamond stability field (Stachel and Luth, 2015) imply speciation of CHO fluids near the "water-maximum", i.e. fluids consisting principally of H_2O with minor CH_4 and CO_2 (blue field in Fig. 1). Because in this model oxygen fugacity is not imposed on the fluid, but rather is dependent on the fluid composition, fluid speciation in Fig. 1 is plotted as a function of the composition of the fluid. Both the fO_2 and the speciation of the fluid are defined therefore by P, T, and the bulk compositional variable O/(O + H), which varies in a C-saturated fluid from zero (for C–H fluids) to one (for C–O fluids).

This new model for diamond formation also has profound impact on how we interpret diamond stable isotope data with respect to possible Rayleigh fractionation processes. Carbon isotope fractionation actually becomes considerably more complex than previously appreciated, as diamond precipitates from fluids containing more than one carbon species and, in most cases, the relative abundances of different carbon species in the fluid evolves during progressive diamond crystallization. For isotopic modelling, the reaction between CO_2 and CH_4 (reaction (1)) is most relevant, as the fluid-imposed redox state of cratonic peridotites places them near the water-maximum (i.e., the last fluid they interacted with was in most cases a near water-maximum fluid; see Fig. 1). Equations to model Rayleigh isotopic fractionation in multi-component systems (RIFMS) were developed by Ray and Ramesh (2000) and applied by Ray (2009) to a problem very similar to diamond precipitation from water-maximum fluids, namely crystallization of graphite from water-dominated, mixed CO_2–CH_4 fluids (with CO_2 being the dominant carbon species in the fluid). The RIFMS approach is, however, applicable to a much wider range of stable isotope systems (Ray and Ramesh, 2000) and problems, such as the C isotope evolution in other planets or the C-isotope record of the early Earth.

Here we apply the RIFMS equations (online supplement 1) to diamond precipitation from water-maximum fluids with initial X_{CO_2} (molar CO_2/[$CO_2 + CH_4$]) in those fluid ranging from 0.10 to 0.89. The latter value corresponds to the position of the EMOD buffer (Fig. 1), which provides an upper limit in X_{CO_2}, and by extension fO_2, for diamond (and CO_2) stability in depleted peridotite (harzburgite). Our goal is to determine if the calculated trends and ranges in the carbon isotope composition of diamond precipitates can be reconciled with existing data sets.

2. Modelling

For RIFMS modelling of reaction (1), CH_4 and CO_2 each contribute 1 atom of carbon to the formation of diamond. The RIFMS calculations themselves then have the following unknowns: (1) the temperature-dependent carbon isotope fractionation factors (α-values) between diamond and CO_2 and CH_4 and CO_2 (if CO_2 is the dominant carbon species in the fluid), or diamond and CH_4 and CO_2 and CH_4 (if CH_4 is dominant); (2) the initial molar ratio (CO_2/CH_4) of the two carbon species in the fluid; and (3) the initial carbon isotope composition of the fluid. The spreadsheet used for the calculations is provided as an online supplement (RIFMS.xlsx).

The required fractionation factors were obtained as follows: Fractionation factors involving CO_2 were derived from the calculations of C-isotope reduced partition function ratios (β-values) for the CO_2 molecule by Chacko et al. (1991). Table 1 gives the coefficients of a 6th-order polynomial equation that fits those CO_2 β-value calculations done for a broad range of temperatures. An