A secretive mechanical exchange between mantle and crustal volatiles revealed by helium isotopes in $^{13}$C-depleted diamonds

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**Abstract**

Fluid inclusions trapped in fast-growing diamonds provide a unique opportunity to examine the origin of diamonds, and the conditions under which they formed. Eclogitic to websteritic diamondites from southern Africa show $^{13}$C-depletion and $^{15}$N-enrichment relative to mantle values ($\delta^{13}$C = -4.3 to -22.2 ‰ and $\delta^{15}$N = -4.9 to +23.2 ‰). In contrast the $^3$He/$^4$He of the trapped fluids have a strong mantle signature, one sample has the highest value so far recorded for African diamonds (8.5 ± 0.4 R$_\odot$). We find no evidence for deep mantle He in these diamondites, or indeed in any diamonds from southern Africa. A correlation between $^3$He/$^4$He ratios and $^3$He concentration suggests that the low $^3$He/$^4$He are largely the result of ingrowth of radiogenic $^4$He in the trapped fluids since diamond formation. The He-C-N isotope systematics can be best described by mixing between fluid released from subducted altered oceanic crust and mantle volatiles.

The high $^3$He/$^4$He of low $\delta^{13}$C diamondites reflects the high $^3$He concentration in the mantle fluids relative to the slab-derived fluids. The presence of post-crystallisation $^4$He in the fluids means that all $^3$He/$^4$He are minima, which in turn implies that the slab-derived carbon has a sedimentary organic origin. In short, although carbon and nitrogen stable isotope data show strong evidence for crustal sources for diamond-formation, helium isotope results reveal an unambiguous mantle component hidden within a strongly $^{13}$C-depleted system.

**Introduction**

Placing diamond-formation into context of large scale tectono-thermal processes, such as subduction and plume-lithosphere interaction, is fundamental to understanding the deep terrestrial carbon cycle (Shirey et al., 2013). Diamond is a chemically simple mineral comprised largely of C and trace N (~0.025 %) incorporated as single nitrogen atoms substituting for carbon (Kaiser and Bond, 1959). The origin of diamond-forming fluids is commonly addressed using the stable isotope values of carbon and nitrogen, where coupled $\delta^{13}$C-$\delta^{15}$N values can indicate diamond growth from mantle-derived fluids (Cartigny et al., 2014). However, many datasets require the contribution of crustal sources for the C and/or N, such as eclogitic diamonds from Dachine (Smith et al., 2016). Sometimes, C-N isotope systematics do not fully resolve the origin of the diamond-forming fluids. For instance, eclogitic diamonds from Jwaneng (Cartigny et al., 1998) and Orapa (Cartigny et al., 1999) show crust-like low $\delta^{13}$C values yet have mantle-like negative $\delta^{15}$N values (Fig. 1), and C and N isotope systems can be decoupled during diamond-formation (Mikhail et al., 2014; Hogberg et al., 2016).

Diamonds can trap fluid during their growth, either along the diamond fibres, between interlocking polycrystalline grains, and surrounding diamond-hosted mineral inclusions (Navon et al., 1988; Jacob et al., 2014). As well as providing the only direct samples of metasomatic fluids from the mantle (Weiss et al., 2015), the trapped fluids enable the application of noble gas isotope tracers to resolve the origin of diamond-forming fluids (Burgess et al., 1998; Gautheron et al., 2005; Broadley et al., 2018; Timmermann et al., 2018, 2019a,b). Here we combine C-N isotope and nitrogen abundance data from southern African diamondites with He isotope data from micro-inclusions in the same sample to investigate the origin of carbonaceous fluids in the mantle. These new data shed light on the number of discrete sources required for the generation of carbonaceous high-density fluids responsible for diamond-formation in the SCLM.

**Samples and Methods**

Three main diamond types are recognised; monocrystalline, fibrous and polycrystalline. The latter, also known as diamondites, are a mixture of diamond intergrown with silicates and...
Carbon and Nitrogen Geochemistry

$^{13}$C values range from -4.3 to -22.2 ‰ and $^{15}$N range from -4.9 to +23.2 ‰ (Fig. 1). Although they overlap, the southern African diamonds have lower mean $^{13}$C (-19.8 vs. -12.1 ‰) and higher average $^{15}$N values (+10.6 vs. +5.2 ‰) than the Orapa diamonds. There is no systematic relationship between C or N isotope values and the silicate paragenesis, consistent with previous observations (Mikhail et al., 2019). Although mantle-like C and N isotope values are recorded, no sample plots in the mantle field (Fig. 1). Diamonds show $^{13}$C-depletion and $^{15}$N-enrichment relative to mantle values. The Orapa diamonds have a more pronounced $^{13}$C-depletion and $^{15}$N-enrichment when compared to the eclogitic and peridotitic monocrystalline diamonds from the same kimberlite (Fig. 1). These data indicate crustal fluids sourced from subducted oceanic sediments or altered oceanic crust (Thomazo et al., 2009). Nitrogen concentrations range from 8–1389 ppm and do not correlate with $^{13}$C or $^{15}$N, consistent with previous observations (Mikhail et al., 2013, 2014, 2019).

Helium Isotopes

The $^3$He/$^4$He ratios range from 0.06 to 8.5 $R_a$, overlapping, but extending, the range previously measured in southern Africa diamonds (Fig. 2a). The highest $^3$He/$^4$He in these
diamondites (8.5 ± 0.4 R\textsubscript{a}) exceeds the highest ratios measured in all other diamondites and fibrous diamonds from southern Africa (Fig. 2a). It is higher than values typical of SCLM (6.1 ± 1 R\textsubscript{a}; Gautheron \textit{et al.}, 2005) and modern kimberlite from southern Africa (4.2 R\textsubscript{a}; Brown \textit{et al.}, 2012), and overlaps the present day convecting upper mantle (8 ± 1 R\textsubscript{a}; Graham \textit{et al.}, 2014).

The southern Africa diamondites formed between kimberlite emplacement and craton stabilisation (91 to >3000 Ma; Gurney \textit{et al.}, 2010). The highly aggregated nitrogen in diamondites is consistent with long mantle residence times (Mikhait \textit{et al.}, 2019), which implies ages far greater than 91 Ma. This leaves open the likelihood that 4\textsuperscript{He} produced by alpha decay of U and Th in the fluid, or recoil of 4\textsuperscript{He} into the fluids, has decreased the 3\textsuperscript{He}/4\textsuperscript{He} of the ancient mantle, as opposed to evidence for 3\textsuperscript{He}/4\textsuperscript{He} ingrowth; the highest 4\textsuperscript{He} ratio of the mantle has reduced over time (3\textsuperscript{He}/4\textsuperscript{He} ratios (>10 R\textsubscript{a}) in all other diamondites and fibrous diamonds from southern Africa (Fig. 2a). This suggests that there is no genetic link between the fibrous diamonds and diamondites, and they likely formed in different mantle domains or from isotopically distinct sources.

A mantle origin for the helium trapped in the diamondite fluids is incontrovertible (Fig. 2a), but the incorporation mechanism(s) for He into the high density fluids (HDF) is less clear. Possible mechanisms include the assimilation of He from grain boundaries or small volume mantle melts initiated by the expulsion of slab-derived fluids into the mantle wedge or SCLM. Resolving the origin of the mantle He is hampered by the post-formation ingrowth of radiogenic 4\textsuperscript{He}, and because the 3\textsuperscript{He}/4\textsuperscript{He} ratio of the mantle has reduced over time (e.g., Porcelli and Elliot, 2008). The uncertainty in the diamond age and the He isotope evolution of the mantle makes drawing firm conclusions regarding the source of the mantle He problematic. One prevailing view posits that the southern African kimberlites originate at the edges of large heterogeneities at the core-mantle boundary (Torsvik \textit{et al.}, 2010). This should be evident from high 3\textsuperscript{He}/4\textsuperscript{He} (e.g., Stuart \textit{et al.}, 2003) in kimberlites. In contrast to Brazilian diamonds (Timmermann \textit{et al.}, 2019b), the absence of 3\textsuperscript{He}/4\textsuperscript{He} above Phanerozoic upper mantle values in fluid-rich diamonds from southern Africa rules likely reflects the formation of the diamonds prior to the generation of the kimberlite melts, and post-formation isolation from kimberlite fluids. Furthermore, it is conceivable that high 3\textsuperscript{He}/4\textsuperscript{He} ratios (>10 R\textsubscript{a}) in some samples (e.g., Siberian fibrous diamonds; Bradley \textit{et al.}, 2018) might reflect the higher 3\textsuperscript{He}/4\textsuperscript{He} of the ancient mantle, as opposed to evidence in sedimentary rocks (Thomazo \textit{et al.}, 2009). Furthermore, the prevalence of eclogitic to websteritic silicate inclusions/intergrowths in these diamondites further supports a recycled basaltic component (Mikhait \textit{et al.}, 2019). These observations contrast strongly with the fibrous diamonds which, although they also contain a high density of trapped fluids with evidence of recycled material based on lithophile element geochemistry and Sr-isotopes (Weiss \textit{et al.}, 2015), they commonly show C and N isotope values that are indistinguishable from mantle values (see Fig. 2a,b). Despite significantly lower 3\textsuperscript{He} concentrations, they are thus more likely to be affected by radiogenic 4\textsuperscript{He} ingrowth; the highest 3\textsuperscript{He}/4\textsuperscript{He} southern African diamondites are higher than the highest values measured in fibrous diamonds from southern Africa (Fig. 2a). This suggests that there is no genetic link between the fibrous diamonds and diamondites, and they likely formed in different mantle domains or from isotopically distinct sources.

\section*{Tracing the Origin of Diamondite-forming Volatiles}

Mixing lines in Figure 2b are drawn between oceanic crust-derived fluids with δ\textsubscript{13}C = -20 and -30 ‰, and 3\textsuperscript{He}/4\textsuperscript{He} = 0.01 R\textsubscript{a}, and mantle-derived fluids with δ\textsubscript{13}C = -5 ‰ and 3\textsuperscript{He}/4\textsuperscript{He} = 9 R\textsubscript{a}. The mantle 3\textsuperscript{He}/4\textsuperscript{He} end member is slightly higher than the present day upper asthenosphere and lithosphere mantle values, reflecting the temporal evolution of 3\textsuperscript{He}/4\textsuperscript{He} in the mantle (Porcelli and Elliot, 2008).

The spread of data can be explained by mixing between He-rich, high 3\textsuperscript{He}/4\textsuperscript{He} mantle source (δ\textsubscript{13}C = -5 ‰) and a He-poor, low 3\textsuperscript{He}/4\textsuperscript{He} crustal component (δ\textsubscript{13}C between -15 and -25 ‰). This is strongly supported by the 3\textsuperscript{He}/4\textsuperscript{He}-enrichment in the 13\textsuperscript{C}-depleted samples which best matches altered oceanic crust (Cartigny \textit{et al.}, 2014) or organic material hosted in sedimentary rocks (Thomazo \textit{et al.}, 2009). Furthermore, the prevalence of eclogitic to websteritic silicate inclusions/intergrowths in these diamondites further supports a recycled basaltic component (Mikhait \textit{et al.}, 2019). These observations contrast strongly with the fibrous diamonds which, although they also contain a high density of trapped fluids with evidence of recycled material based on lithophile element geochemistry and Sr-isotopes (Weiss \textit{et al.}, 2015), they commonly show C and N isotope values that are indistinguishable from mantle values (see Fig. 2a,b). Despite significantly lower 3\textsuperscript{He} concentrations, they are thus more likely to be affected by radiogenic 4\textsuperscript{He} ingrowth; the highest 3\textsuperscript{He}/4\textsuperscript{He} southern African diamondites are higher than the highest values measured in fibrous diamonds from southern Africa (Fig. 2a). This suggests that there is no genetic link between the fibrous diamonds and diamondites, and they likely formed in different mantle domains or from isotopically distinct sources.

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for the role of mantle plumes in the generation of shallow diamonds. While the highest diamondite $^3\text{He}/^4\text{He}$ ratios are above modern SCLM values, they do not allow a distinction to be made between an ancient sub-continental lithospheric or a convecting upper asthenospheric mantle source. That said, the absence of $^3\text{He}/^4\text{He}$ above Phanerozoic upper mantle values in fluid-rich diamonds from all southern Africa rules out a requirement for deep mantle fluids in the generation of diamonds in the SCLM. Diamondites from southern Africa crystallised from HDFs where the C originates from crustal and mantle sources, the N is mostly slab derived, likely from a subducted sedimentary organic component, but the He is largely derived from the upper mantle.

The carbon and nitrogen isotope data (Fig. 1) are consistent with prevailing models for diamondite-formation, whereby high density fluid from a subducting slab interacts with the SCLM (Mikhail et al., 2013, 2019; Jacob et al., 2000, 2014). Mechanically, this journey provides an opportunity for the exchange of material between a subducted fluid acting as a mobilising agent (HDF) with solid residual mantle rocks (illustrated in Fig. 3). This physical interaction can assimilate mantle volatiles into the HDF resulting in hybridisation (where the HDF is now comprised of subducted + mantle volatiles). If the mantle component in the subduction-derived HDF is small, then the diamond-forming media might not reveal this assimilated mantle component in $\delta^{13}\text{C}$-$\delta^{15}\text{N}$ space (e.g., as shown for most samples in Fig. 1). For example, if the subducted carbon has $\delta^{13}\text{C} = -25\%$ and assimilated 10\% mantle carbon ($\delta^{13}\text{C} = -5\%$) with most of the nitrogen provided by the subducted source ($\delta^{15}\text{N} > 0\%$) then the resulting hybrid would have a $\delta^{13}\text{C}$ value of -23\% and positive $\delta^{15}\text{N}$. Such $\delta^{13}\text{C}-\delta^{15}\text{N}$ values do not suggest mixing between mantle and crustal volatiles because they are within the range of crustal organic carbon and distinct from the canonical mean mantle values for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (-5 ± 3\%; Cartigny et al., 2014; Mikhail et al., 2014). However, if the $^{13}\text{C}$-depleted HDF assimilated 50\% mantle carbon and 100\% mantle helium, then the resulting hybrid would have a $\delta^{13}\text{C}$ value of -15\% and $^3\text{He}/^4\text{He} > 1\text{Ra}$. This scenario matches the data of samples Dia030 (southern Africa) and ORF57 (Orapa) which show elevated $^3\text{He}/^4\text{He}$ ratios of 8.5 and 7.5 Ra with corresponding $\delta^{13}\text{C}$ values (-16.6\%; Fig. 2b).

We argue that the C-N isotope data commonly identify a mix of multiple sources. In the case of the southern African and Orapa diamondites, the $\delta^{13}\text{C}-\delta^{15}\text{N}$ systematics reveal that the subducted component dominates over the mantle component (Fig. 1). However, the discrete, but important, mantle component is revealed in the fluid-hosted helium isotope data. The higher $^4\text{He}$ concentration of the mantle fluids compared to slab-derived fluids means that the helium isotopes trace small contributions of mantle-derived volatiles better than C or N isotopes. For example, samples DIA058B (southern African) and ORF143 (Orapa) show elevated $^3\text{He}/^4\text{He}$ ratios of 3.9 and 1.6 Ra with correspondingly low $\delta^{13}\text{C}$ values of -19.1 and -19.9\% (Fig. 2b). Ergo, helium reveals what carbon and nitrogen cannot. When the carbon and nitrogen stable isotope data show strong evidence for crustal sources for diamond formation (Fig. 1), the helium isotopes reveal an unambiguous mantle component hidden within strongly $^{13}\text{C}$-depleted diamond (Fig. 2b). This observation speaks to the mechanics of fluid migration through the SCLM. Our data require that subducted material percolates though ambient mantle en route to the SCLM and results in the mechanical re-mobilisation of primary mantle volatiles (Fig. 3). These data further enhance the notion that the volatile-element components within a diamond-forming HDF do not always share a common origin, and indeed, the C-N-He isotopic systems preserved in mantle diamonds record distinct processes and should not be considered coupled isotopic systems, by default.

![Figure 3 Cartoon illustrating the model discussed in the text. Not to scale.](image-url)
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Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/articlei923.

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