Origin of kimberlite from the base of the upper mantle

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Abstract:

Kimberlite is characterized by explosive eruption powered by excess carbon dioxides (CO$_2$)$^1$ and water$^2$. Given that diamond is the dominant stable phase of carbon in the upper mantle$^3$, it is obscure where does the excess CO$_2$ in kimberlite has come from. Here we show that ferric iron oxidizes diamond at 1900K, 20GPa and 2000K, 25GPa, forming CO$_2$. The lower mantle is dominated by bridgmanite, which is rich in ferric iron$^4$. Bridgmanite decomposes once it is brought to the upper mantle, releasing extra ferric iron. Therefore, the oxidation of diamond may have been popularly occurring at the base of the upper mantle, forming CO$_2$-rich carbonated domains that are the main source of kimberlite. The rising kimberlitic magma reaches the lithosphere mantle of thick cratons before it crosses the solidus line of mantle peridotite, and thus keeps its volatile-rich nature that drives explosive eruptions. When the lithospheric mantle is thinner than ~140 km, kimberlite changes into much less explosive magmas due to partial melting of mantle peridotite, and, consequently, entrained diamond is mostly oxidized during the magma’s slower ascension.
Main Text

It has long been established that diamondiferous kimberlites are exclusively distributed in ancient lithospheric mantle, thicker than 140 kilometers (Figure 1), which transport diamond to the surface through volatile-charged highly explosive kimberlite magmas. However, cratons are old (e.g., >2.5 billion years), whereas kimberlites are young (mostly < 0.6 billion years), suggesting that kimberlite is not necessarily coupled with cratons. Plate reconstruction shows that most of the kimberlites were located above one of the two large low shear wave velocity provinces in the lower mantle, suggesting their genetic connections with mantle plumes. Kimberlite has several percent of CO$_2$ and also H$_2$O, which are the main components that make kimberlite explosive. However, cratons have been highly devolatized, such that the roots of ancient cratons are generally dry, which is essential to maintain cratons stable for billions of years. Moreover, carbonate cannot be stored in the asthenospheric mantle at depths shallower than 300 km (Figure 2), because the solidus line of carbonated peridotite is lower than the mantle geotherm.

Diamond, rather than CO$_2$, is the dominant carbon species in the upper mantle. Therefore, conventional models have difficulties to explain the source of large quantities of excess CO$_2$ in kimberlites. Previous studies showed that oxidation of diamond through redox melting is required to form CO$_2$ in mid-ocean ridge basalts. Under normal mantle condition, redox melting occurs at depths between 150 to 120 km. For mid-ocean ridge basalts, 30 ppm of C in average should have been oxidized to carbonate at the expense of 3% of Fe$^{3+}$/Fe$_{total}$ in the upper mantle. However, such redox melting has complications to explain the high abundance of carbonate and excess CO$_2$ in kimberlite.
First of all, formation of kimberlite through redox melting will require ferric iron abundance more than 100 times higher than the estimated value of the upper mantle. Second, the oxygen fugacity decreases with increasing depths\textsuperscript{20,21}, and diamond is the stable carbon species deeper than 170 km in the upper mantle. Therefore, carbonate-induced melting may occur but only at shallow depths of 150-120 km\textsuperscript{3}, whereas kimberlite forms mostly deeper than 140 kilometers\textsuperscript{3,5}. In addition, both the reductant (diamond) and the oxidizing agent (ferric iron) are solid or hosted in solid minerals that are not readily mobile. It is difficult to concentrate the scarce diamond into kimberlite during dispersed small degree redox melting. More importantly, the key point of redox melting is that elemental carbon (diamond or graphite) is oxidized within upwelling. Therefore, the degree of redox melting increases with increasing upwelling distance. In this case, the thicker the lithosphere, the less the redox melting, i.e., melts underneath cratons should have less CO\textsubscript{2}. This is exactly the opposite of the distribution of kimberlite.

The best place to oxidize diamond is the base of the upper mantle. The lower mantle is rich in ferric iron because of ferrous iron disproportionation that forms native and ferric iron\textsuperscript{4}. Native iron is much denser and thus sinks towards the core. Ferric iron is hosted in bridgmanite, the dominant mineral in the lower mantle with high ferric iron contents (up to >60\%)\textsuperscript{4,21}. Under the pressure-temperature (P-T) conditions of the upper mantle, it transforms into ringwoodite, which has essentially no ferric iron, and releasing ferric iron that reacts with the surrounding mantle. During deep plate subduction that penetrates across the 660 km discontinuity\textsuperscript{22}, some of the bridgmanite is pushed up into the upper mantle through compensational background upwelling, and then decomposes. Therefore, diamond
tends to be oxidized by ferric iron at the base of the upper mantle, forming a CO$_2$ rich carbonated layer.

To test this model, we performed experiments in a laser-heated diamond anvil cell (DAC) at 20 GPa, 1900 K and 25 GPa, 2000 K (Methods). A mixture of analytically pure Fe$_2$O$_3$ and graphite reagent with a mass ratio of 7:3 was used as the starting materials. We investigated the redox reaction between Fe$_2$O$_3$ and graphite under the P-T conditions of the bottom of the upper mantle and identified the phase assemblages of the run products by Raman spectroscopy. Raman spectroscopy of the run products shows that CO$_2$-IV coexists with Fe$_3$O$_4$ under 20-25 GPa and 1900-2000 K, indicating that the diamond is oxidized by ferric iron and generated CO$_2$-IV (Figure 3).

The reaction equation is as follows:

$$6\text{Fe}_2\text{O}_3 + \text{C} = 4\text{Fe}_3\text{O}_4 + \text{CO}_2\text{-IV} \quad (1)$$

According to Equation (1), the total amount of cation decreases while the total amount of anion increases during the reaction, resulting in excess CO$_2$.

High-pressure experiments show that CO$_2$ is stable in the mantle under pressures higher than 9 GPa$^{18}$. It appears as CO$_2$-IV at the base of the upper mantle. Our experiment results suggest that there should be carbonated domains with excess CO$_2$-IV at the base of the upper mantle, which is the source of kimberlites and diamond deposits.

This model is supported by Sr, Nd isotopes. Kimberlites are characterized by highly varied Sr and Nd isotopes compared to silicate rocks. Three endmembers are recognized (Figure 4). In addition to the depleted mantle and the continental crust endmembers, kimberlites have a unique endmember with strikingly low $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd (LSN hereafter). All the kimberlites plot in the mixing field among these endmembers.
Considering that the cratonic mantle is highly depleted in terms of Sr-Nd isotopes, the Sr-Nd isotopes suggest that a large proportion of kimberlites were not originated from the cratonic mantle.

The continental crust endmember may be plausibly explained by recycling of subducted sedimentary carbonates, whereas the depleted mantle endmember is attributed to assimilation of the depleted mantle by kimberlites during the upwelling.

The low $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ (LSN) endmember mantle domains have not been identified in silicate rocks, suggesting that a considerable portion of kimberlites were originated from an unique mantle domain that silicate magmas have rarely sampled. Interestingly, carbonatite also has such an endmember, indicating that this endmember involves only in carbonatic magmas, but not in silicate magmas.

Partial melting of mantle peridotite starts at depths of ~ 150 kilometers, depending on temperatures. In contrast, partial melting of carbonated mantle peridotite may start at depths of ~300 kilometers under the current mantle geotherm. It starts to melt even in the lower mantle at elevated temperatures, e.g., mantle plume (Figure 2). Therefore, the most straightforward explanation is that the LSN source is deep.

The LSN isotope characteristics require ancient source(s) with very low Rb/Sr and Sm/Nd ratios. Garnet strongly enriches heavy rare earth elements, with high Sm/Nd, so does majorite. Therefore, ringwoodite formed in the presence of majorite should have low Sm/Nd. It transforms into bridgmanite in the upper most lower mantle, while majorite is stable. Consequently, these bridgmanite has low Sm/Nd in the presence of majorite. Similarly, hollandite is stable in the transition zone and the lower mantle. Considering that hollandite is a potassium mineral, it should have high Rb/Sr ratios. Therefore,
bridgmanite formed in the presence of hollandite should also have lower Rb/Sr ratios. Once these bridgmanite is pushed into the upper mantle, it decomposes, oxidizes diamond, and forms the LSN endmember of kimberlite.

Our model also plausibly explains the close association of kimberlites with mantle plumes\(^7\). When an ascending mantle plume head approaches the base of the upper mantle, carbonated mantle domains with excess CO\(_2\) is the first to be partially melted, forming explosive kimberlite melts that may carry diamond with it. At depths below 410 km, diamond is less dense than mantle peridotite in solid state. Therefore, during the formation and upward migration of kimberlite, diamond tends to be preferentially concentrated above the coexisting mantle peridotite, such that it is easier to be sampled by the kimberlite melt (Figure 5).

The upwelling of hot kimberlite melt may cause partial melting of mantle peridotite at depths of ~ 140 km, depending on the mantle temperature. Under cratons that are thicker than 140 km, kimberlite reaches the base of thick refractory cratons without significant partial melting of mantle peridotite, such that it has a better chance to keep its explosive nature that brings diamond to the surface. This plausibly explains the distribution of kimberlite and carbonatite as well as alkalic basalt (Figure 1). Kimberlite is exclusively distributed within cratons thicker than 140 km at the time of eruption\(^{24,25}\). In contrast, carbonatite and alkalic basalt are more abundant in places having thinner lithosphere.

In non-craton regions, the lithospheric mantle is thin and less refractory. Mantle peridotite starts to melt as kimberlite melt ascends to depths of less than ~140 km. Consequently, kimberlite melts are transformed gradually into carbonatite, and then to alkali basalts\(^{26,27}\), and even to normal basalts. Meanwhile, CO\(_2\) reacted with the mantle,
scavenging Na, Mg and Sr, etc. These magmas are far less explosive, and thus ascend more slowly. Meanwhile the density of diamond is higher than mantle peridotite and melts at depths shallower than 410 km. As a result, it sinks to the bottom of the melt. Limited diamond left in the melt should be transformed to graphite when it passes through the graphite stability field, and may consequently be oxidized to carbonate through redox melting\(^3,28\).

If the plume head is stronger and rises further, partial melting of carbonated peridotite may also occur at depths of > 140 km, forming carbonatite under cratons (Figure 1). Large igneous provinces form when the plume head successfully penetrates the whole upper mantle, causing large degrees of partial melting\(^29,30\). This explains the fact that large igneous provinces are often proceeded by carbonatite\(^31\).

According to our model, kimberlite originates mainly at the base of the upper mantle, with abundant lower mantle material carried up through background upwellings. This plausibly explains inclusions of lower mantle origin\(^32\). It also explains the high water contents of kimberlite\(^2,18\). Previous studies on ringwoodite inclusions in diamond suggested that the transition zone is hydrous with H\(_2\)O content of about 1 weight percent\(^33,34\). Therefore, kimberlite may acquire water as it ascending across the transition zone.

At depths of less than 100 km, kimberlite may react with the mantle peridotite on its journey passing through the thick cratonic lithosphere\(^35\), forming olivine and clinopyroxene at the expenses of orthopyroxene\(^1,36\), providing additional excess CO\(_2\) that further promotes the explosive kimberlite. It also plausibly explains the absence of orthopyroxene in kimberlite\(^1\).
This model also feasibly explains the occurrence of diamond and ultrahigh pressure minerals in ophiolite\textsuperscript{37,38}. Oceanic lithosphere is generally thinner than 90 km. As mentioned above, silicates start to melt as kimberlite melt ascends to depths of <140 km, such that kimberlite melts tend to be transformed into basalts. Consequently, diamond carried up by kimberlite disappears due to transformation and oxidation. However, in cases where the kimberlite was located underneath a spreading ridge, and thus was much easier to erupt to the surface, there still could be diamond and other ultrahigh pressure phases left, mostly likely as inclusions. This plausibly explains the occurrence of diamond in ophiolites.
Sample preparation and pressure determination

Powder of hematite (99.99%, Alfa Aesar) and graphite (99.99%, Alfa Aesar) was mixed at a mass ratio of 7:3 and ground in an agate mortar for 6 hours.

Boehler-Almax diamond anvils with flat culet diameters of 300 μm were used for the experiments. The starting material was pre-compressed into disks of ~15 μm thickness. A thin disk of the starting material was then sandwiched between two layers of quartz which serve as both pressure transmitting medium and thermal insulation and placed in a rhenium (Re) gasket hole preindented to a thickness of about 35 μm. To avoid potential moisture contamination in the sample chamber, before sealing the sample chamber, the DAC was stored in an oven at 120°C for 12 hours. The pressures at room temperature were determined based on the Raman shift of a diamond anvil\textsuperscript{39}.

Raman experiments in laser-heated DACs

High P-T Raman experiments were performed at the Center for High Pressure Science & Technology Advanced Research (HPSTAR). The samples were heated by a Ytterbium fiber laser on both sides\textsuperscript{40}. The heating temperature on both sides of the heated sample was determined by fitting the visible part of the gray-body radiation with Planck radiation function\textsuperscript{41,42}. The uncertainty of temperature in the whole heating experiments is ±50K.

The Renishaw 2000 type Raman is equipped with a charge-coupled device detector, 2400 line mm\textsuperscript{-1} diffraction grating and holographic filter. The zero shift was calibrated using a 520 cm\textsuperscript{-1} single crystal of silicon. The excitation light was 532 nm, and the acquisition time of each Raman spectrum was 5 minutes to ensure the quality of data.
analysis. Gaussian + Lorentzian functions of Peakfit software (Systat Software, San Jose, CA) were used to fit the Raman data. We observed many overlapping peaks in a typical powder Raman pattern of the run products. To identify the phases, we applied the characteristic peaks of these phases for classification.

Competing interests: The authors declare no competing interests.
Figure 1. The distribution of kimberlite and carbonatite all over the world. All the kimberlites are distributed in craton thicker than 140 km. In contrast, carbonatite is not selective to lithosphere thickness. Data from the GEOROC database.
Figure 2. Density and temperature profiles of the mantle. The solidus line of carbonated mantle peridotite (green dot dash line) is lower than the solid adiabat of the mantle (green solid line) at depths shallower than 300 km\textsuperscript{14}. This suggests that no carbonate can survive at the bottom of the lithospheric mantle. Diamond (orange solid line) is denser than peridotite melt (orange dotted line) at shallow depths, but is less dense in the lower mantle. The density crossover is close to the 660 km discontinuity. Therefore, diamond has accumulated at the base of the upper mantle in the Magma Ocean. This diamond layer has been oxidized by bridgmanite upwelled from the lower mantle, forming carbonated peridotite\textsuperscript{43} with excess CO\textsubscript{2}.
Figure 3 The run products and CO$_2$-IV Raman pattern at several high-pressure conditions from this study and previous studies$^{44-46}$. Raman spectra of the run products of this study show characteristic peaks of CO$_2$-IV, 108 cm$^{-1}$ at 20 GPa and 134 cm$^{-1}$ at 25 GPa, although there are many overlapping peaks between Fe$_2$O$_3$ and CO$_2$-IV in high pressure Raman spectra. Previous studies found that CO$_2$ generated CO$_2$-IV under experimental conditions of 20-25 GPa and 1900-2000 K. All Raman shift to the right with increasing pressures. The Raman shift range of 100-400 cm$^{-1}$ is consistent with the previous research of CO$_2$-IV$^{44-46}$. The Raman peaks of 462 cm$^{-1}$, 553 cm$^{-1}$, 707 cm$^{-1}$ at 20 GPa and 492 cm$^{-1}$ at 25 GPa of this study are consistent with the high-pressure Raman pattern of Fe$_2$O$_3$$^{47}$ (orange triangle), and the Raman peaks of 793 cm$^{-1}$ at 20 GPa and 865 cm$^{-1}$ at 25 GPa are consistent with the high-pressure Raman pattern of Fe$_3$O$_4$$^{48}$ (blue star), and the Raman peaks of 238 cm$^{-1}$ and 521 cm$^{-1}$ at 20 GPa and 246 cm$^{-1}$ at 25 GPa are consistent with the high-pressure Raman pattern of stishovite$^{49}$ (green diamond). In summary, the experimental results show diamond is oxidized by ferric iron, forming CO$_2$-IV.
Figure 4. Diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ for global kimberlite. Sedimentary carbonates are also shown in the Figure (grey square). Kimberlites have highly varied and mostly enriched isotopes compared to silicate rocks\textsuperscript{50}, suggesting that they were originated from special enriched mantle domains that have not been sampled by silicate melts. This clearly excludes cratonic mantle, which is depleted in terms of Sr-Nd isotopes. The Sr and Nd isotope compositions of kimberlites and sedimentary carbonates are obtained from the GEOROC database.
Figure 5 (a) Kimberlite formation model. When a mantle plume approaches the base of the upper mantle, previously formed and stabilized CO$_2$ is activated, followed by partial melting of carbonated mantle peridotite and water rich phases, forming kimberlite. (b) Formation of large igneous province. Large igneous provinces form when the plume head penetrates the transition zone, with most of the melting occurred at shallow depths, forming carbonatite and basalts. Both carbonatites and large igneous province magmas are not as explosive as kimberlite, such that they erupt more slowly, losing diamond during ascent.
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