Carbonatitic Melts and Their Role in Diamond Formation in the Deep Earth

Suzette Timmerman[1], Anna V. Spivak[2], and Adrian P. Jones[3]

1 University of Alberta Department of Earth and Atmospheric Sciences Edmonton, Alberta, Canada E-mail: suzette@ualberta.ca

2 Russian Academy of Sciences, D.S. Korzhinskii Institute of Experimental Mineralogy Russia E-mail: spivak@iem.ac.ru

3 University College London Department of Earth Sciences United Kingdom E-mail: adrian.jones@ucl.ac.uk

Carbonatitic high-density fluids and carbonate mineral inclusions in lithospheric and sub-lithospheric diamonds reveal comparable compositions to crustal carbonatites and, thus, support the presence of carbonatitic melts to depths of at least the mantle transition zone (~410–660 km depth). Diamonds and high pressure–high temperature (HP–HT) experiments confirm the stability of lower mantle carbonates. Experiments also show that carbonate melts have extremely low viscosity in the upper mantle. Hence, carbonatitic melts may participate in the deep (mantle) carbon cycle and be highly effective metasomatic agents. Deep carbon in the upper mantle can be mobilized by metasomatic carbonatitic melts, which may have become increasingly volumetrically significant since the onset of carbonate subduction (~3 Ga) to the present day.

Keywords: carbonatitic melt; diamond; viscosity; metasomatism; carbon cycle; carbonate

INTRODUCTION

Diamonds provide direct samples of the mantle and most are formed in the sub-continental lithospheric mantle at depths of ~140–220 km. Uncommon “superdeep” diamonds with higher pressure inclusions are interpreted to have formed in the lower parts of the upper mantle and upper parts of the lower mantle, at ~300–800 km depth (Stachel et al. 2005). Diamonds are delivered to the surface by kimberlitic magmas and associated magmas, such as orangeites, lamproites, and lamprophyres: volatile-rich, fast-ascending, low-degree mantle melts. Carbonatite rocks are igneous rocks with >50 vol% primary carbonate minerals (Kamenetsky et al. 2021 this issue and references therein); their parental mantle-derived carbonatitic melts lie on a chemical continuum with kimberlitic melts (kimberlites have higher Mg and Si but lower Ca and CO2). Carbonatite rocks are found in continental settings, with 75% being emplaced within 600 km of cratons (Humphreys-Williams and Zahirovic 2021 this issue), and they have been spatially connected to kimberlites (Snap Lake, Canada; Premier, South Africa) and to ultramafic lamprophyres (Alnö, Sweden; Kandalaksha, Russia; Aillik Bay, Canada).

The rare occurrences of diamonds in carbonat ites (Chagatai, Uzbekistan; Dalihu, China) and the widespread finds of carbonate mineral inclusions and carbonatitic high-density fluid (HDF) inclusions in lithospheric and sub-lithospheric diamonds suggest that at least some carbonatitic melts are formed at great mantle depths (>120 km) and are involved in diamond growth.

Here, we review the connection between diamond, carbonatite rocks, and the metasomatic, deep-probing nature of carbonatitic melts in the mantle from the perspectives of both experimental and natural samples. The stability of carbon phases and melts, and diamond formation reactions and their dependence on P, T and fO2 have been studied through thermodynamic models and high pressure–high temperature (HP–HT) multi-anvil and piston-cylinder experiments. Variations in the laboratory starting compositions (CO2, Na2O, K2O, MgO, CaO, FeO contents)—reflecting the major element variations of natural carbonatites—have a significant effect on the peridotite solidus temperature and implied mobility of carbonatitic melt. The major elements, trace elements, and isotopic compositions of carbonatitic HDFs in diamonds and carbonatitic melts overlap.

THE CARBONATITE–DIAMOND CONNECTION

Carbonatitic High-Density Fluids in Lithospheric Diamonds

Diamond can trap both crystalline solids and the parental fluid (the HDF) during growth in the mantle (KleinBenDavid et al. 2009). A range of mantle carbonatitic melt compositions can be inferred from Mg-rich to Fe-rich micro-inclusions of magnesite (MgCO3), siderite (FeCO3), and dolomite in diamonds from different kimberlite localities (Diavik, Northwest Territories, Canada; Panda, Northwest Territories, Canada; Internationalaya, Sakha, Russia). The first recognition of inclusions of alkaline carbonate with water was reported in cloudy and fibrous diamonds from the lithospheric mantle by Navon et al. (1988), whose group subsequently classified HDF compositions into four endmembers: hydrous silicic; low-Mg carbonatitic; high-Mg carbonatitic; and hydrous saline. The low-Mg and high-Mg carbonatitic HDFs bear similarities with carbonatitic melts from HP–HT experiments and will be the main focus for chemical comparison here.

Major and Trace Element Compositions of Carbonatitic Melts

High-density fluid inclusions in diamonds can be used to reconstruct compositions of high-pressure carbonatitic melts. The inclusions are measured unexposed to avoid contamination and loss of the fluid and volatiles: this results in low analytical totals (14 wt% MgO) and, thus, unknown amounts of CO2 and H2O. Water and CO2 contents are reconstructed from Fourier transform infrared (FTIR) spectra and cation (CO3 2–) contents from inclusions measured by electron probe microanalysis (EPMA) and/ or scanning electron microscopy (SEM), and volatiles are proposed to make up ~40 wt% (Navon et al. 1988).

The carbonatitic HDF endmembers in diamonds are rich in Mg, Ca, K; are enriched in incompatible elements relative to primitive mantle compositions; are low in Si and Al; and are low in Sr, Ti, and Y relative to the middle rare earth elements (MREEs) and heavy rare earth elements (HREEs). Low-Mg carbonatitic HDFs have <14wt% MgO. High-Mg carbonatitic HDFs (>14 wt% MgO) have higher Na2O and BaO relative to low-Mg carbonatitic HDFs, on a volatile-free basis (Klein-BenDavid et al. 2009). Although HDF compositions are often compared to solid crustal carbonatite rocks, it is important to remember that the latter are susceptible to late-stage modification by magmatic processes and alteration (Kamenetsky et al. 2021 this volume). Coarse-grained plutonic carbonatites are often cumulate in nature, and carbonatitic melts lose soluble alkalis to hydrothermal, magmatic, or meteoric fluids during cooling. Thus, crustal carbonatites do not represent the compositions of the carbonatitic melts that led to their formation.

As shown in Figure 1A, high-Mg carbonatitic HDFs overlap compositionally with carbonatitic melts formed by partial melting of peridotite in HP–HT experiments, demonstrating that both diamonds and carbonatite rocks can crystallize from comparable liquids. Both low-Mg and high-Mg carbonatitic HDFs show similarities, such as trace element enrichment, with carbonatite rocks and kimberlites (Fig. 1B). The high-Mg carbonatitic HDFs are related to a peridotitic paragenesis and have mostly been found in diamonds from Udachnaya on the Siberian craton, and Kankan on the West African craton. Low-Mg carbonatitic HDFs display a continuous compositional trend with silicic fluids and are associated with an eclogitic paragenesis based on mineral inclusions such as coesite, omphacite, and garnet (pyrope–almandine–grossular with 6–32 wt% CaO and <1wt % Cr_2O_3) within the same diamonds. The high-Mg HDFs exhibit lower alkalis, Zr, Hf, Ti, and Y, and higher Nb, Ta, and Ba–Th–U/alkali, light rare earth element (LREE)/MREE, and LREE/HREE ratios compared to the low-Mg carbonatitic HDFs (Fig. 1B) (Weiss et al. 2009).

Formation Models and Isotopic Insights

Since the discovery of HDFs in diamond by Navon et al. (1988), ideas around the formation of these diamondforming fluids have evolved significantly. Initial models tried to explain the saline–carbonatitic–silicic compositions by evolution from a single parental carbonatitic fluid. Precipitation of carbonate and apatite would drive the fluid into an immiscible field, separating the fluid into separate saline and silicic components (Weiss et al. 2009 and references therein). While experiments in the diopside– carbonate–chloride system confirmed the miscibility gap, the 1) evolution from saline to carbonatitic compositions upon cooling, 2) similar REE incompatibility in carbonate and apatite, but large LREE/HREE variation in HDF, 3) evolution of fluid compositions into different directions in single diamonds (Weiss et al. 2009), and 4) the discovery of the distinction between low-Mg and high-Mg carbonatitic end-members, all argue against an immiscibility and fractionation model to explain all fluid compositions. One current view is that a hydrous saline parental fluid forms through partial melting of subducted basaltic crust and that the product fluid interacts either with hydrous carbonated eclogite to form low-Mg carbonatitic to silicic compositions, or reacts with carbonated peridotite (possibly with magnesite metasomes) to form high-Mg carbonatitic fluids (Weiss et al. 2015).

Partial melts produced in experiments of carbonated eclogite and carbonated peridotite closely resemble the major-element chemistry of low-Mg carbonatitic and high-Mg carbonatitic fluids, respectively (Hammouda and Keshav 2015). Thus, a model of partial melting of carbonated eclogite and peridotite to form carbonatitic melts could explain many compositions observed in HDFs in diamonds (Fig. 1A).

However, most partial melting experiments were carried out with much lower K contents than are observed in HDFs, which are enriched in K compared to carbonatitic melts and carbonatite rocks. Processes other than partial melting are needed to accumulate the higher K and trace element patterns with elevated Ba–U–Th–LREE and depleted Nb–Ta–alkalis (Fig. 1B), such as interaction with, or infiltration of, chloride–potassium-rich (saline) fluids or interaction with a previously metasomatised (now phlogopite-rich) lithosphere. Phlogopite is a mica mineral with high Rb/Sr ratios that evolves to exceptionally high $^{87}Sr/^{86}Sr$ ratios with time due to decay of ^{87}Rb to ^{87}Sr; this characteristic may explain why silicic and saline HDFs in diamonds have higher initial $^{87}Sr/^{86}Sr$ ratios than most carbonatite rocks. Strontium isotope data are extremely limited (only 7 analyses to date), but the majority of existing Sr isotope measurements of high-Mg carbonatitic HDFs are comparable to the low $^{87}Sr/^{86}Sr$ initial ratios of magnesio-carbonatite rocks (Fig. 2) which have Rb/Sr ratios below that of the bulk silicate Earth.

Experimental Constraints on the Conditions of Diamond Growth in the Lithosphere

Not all diamond growth is related to carbonatitic fluids. Diamond formation in the sub-continental lithospheric mantle has been suggested to occur in one of three ways: 1) pH changes during a reaction between CHO fluids and coesite + kyanite-bearing eclogite; 2) redox reactions between CHO fluids and wall rock (eclogite, peridotite, pyroxenite); 3) precipitation from cooling or ascending CHO fluids (Stachel et al. 2017 and references therein). Here, we focus on the mechanisms of diamond formation from carbonatitic melts, which involves reduction of carbonate or CO_2 and cooling of oxidized CHO fluids or low-degree partial melts. The stabilities of the various forms of carbon—either oxidized as solid carbonates, or carbonatitic melts, or as subsolidus CO_2 or CO_3^{2-} fluids; or reduced as for diamond and graphite—are determined by pressure, temperature and fO_2. In the case of a cratonic geotherm, diamond is stable deeper than ~135 km and at conditions more oxidized than +0.1 to +0.6 log units of fO_2 greater than the iron–wüstite redox buffer reaction (given as '+ΔIW', which signifies the log of fO_2 in the sample relative to the log of fO_2 in the iron–wüstite buffer) and more reduced than the fO_2's at which carbonate melts become stable [~ΔIW+2.9 to +4.1, or, equivalently, 1–2 orders of magnitude more reduced than the fayalite–magnetite– quartz (FMQ) redox buffer, or 'ΔFMQ−2 to −1'] (Stagno 2019). The stability of carbonate melts expands to lower $fO_2$with the addition of a silicate component to those melts (Stagno et al. 2020 and reference therein). In the upper part of the mantle (<250 km), fO_2 is broadly determined by Fe^{2+}/Fe^{3+} equilibria in silicate minerals (Fig. 3). However, in harzburgitic environments where fO_2 may be buffered by fluid, diamond precipitation likely does not occur via redox reactions but instead via a reaction between coexisting CO_2 and CH_4 ($\rightarrow$ 2C + $2H_2O$) during cooling of CHO fluids (decreasing the carbon solubility) (Stachel et al. 2017).

Experimental growth of diamond from alkali-carbonate melt is fast. The first HP–HT experiments to be performed on hydrous carbonate compositions showed that CHO fluids are formed and that diamond can both nucleate and grow on seeds in such systems at 5.7 GPa and 1,150–1,420 °C, with alkalis (Na, K) acting as catalysts (Pal'yanov et al. 1999). Further HP–HT carbonate experiments have included silicate components and confirmed that diamond can grow in several different morphologies resembling natural forms—fibrous, coated, polycrystalline, and monocrystalline. The HP–HT experiments performed at 7.7 GPa and 1,500–1,800°C in a graphite-free system with Ca,Mg-carbonate + silica provided direct evidence for the crystallization of diamond via reduction of carbon in carbonatitic melts (Arima et al. 2002).

Sub-Lithospheric Diamond Formation from Carbonatitic Melts

Like some lithospheric mantle diamonds, deeper sub-lithospheric diamonds can contain nano- and micro-inclusions, macro-inclusions, and voidites (faceted void-like defects containing a solid phase). Some nano- and microinclusions in superdeep diamonds (300–800 km depth) were found to be rich in solid molecular nitrogen without evidence for water and carbonate (Navon et al. 2017). Not all superdeep diamonds crystallized from the same fluids or under the same redox conditions, based on observed solidified inclusions of reduced Fe–Ni–C–S liquids in CLIPPIR (which stands for 'Cullinan-like, large, inclusion poor, pure, irregular, resorbed') diamonds and carbonate (identified by FTIR) in cloudy He-bearing transition-zone diamonds. Though major element compositions of such carbonatebearing micro-inclusion-rich parts of diamonds are yet to be determined, trace element abundances and oxygen isotopes (δ18O) of majoritic garnet and Ca,Ti-perovskite mineral inclusions in superdeep diamonds are consistent with crystallization from a low-degree alkali-rich carbonatitic melt derived from subducted and altered oceanic crust in the deeper parts of the upper mantle (Thomson et al. 2016; Regier et al. 2020). Superdeep diamonds with carbonate mineral inclusions confirm the stability of carbonate to depths of the transition zone and perhaps lower mantle.

Experimental Constraints on Conditions of Sub-Lithospheric Diamond Growth

Experimental data on the phase state of simple and multicomponent carbonate systems let us assess the stability of carbonatitic melts at mantle conditions. The HP–HT experiments simulating diamond growth at sub-lithospheric pressures (10–20 GPa) show that both metallic (Fe,Ni) melts and carbonate-melts yield very fast growth (>1 µm/ min) of diamonds that trap melt inclusions (Tomlinson et al. 2011). It has been suggested that fO2 likely decreases with increasing depth in the Earth's upper mantle (Stagno 2019), so that environments more reduced than the lithosphere and upper asthenosphere are expected in the transition zone and lower mantle. The CLIPPIR diamonds are believed to come from such great depth and may derive from metallic liquids. In contrast, oxidized conditions in subducting slabs could provide a very high-pressure environment where crustal-derived carbonates (CaCO3 and MgCO3) might be stable and melt congruently down to depths of the Earth's lower mantle (Litasov et al. 2020).

The HP–HT multi-anvil experiments on mid-ocean-ridge basalt (MORB) eclogites with added CaCO3 indicate that aragonite, magnesite, and alkali-rich carbonates are stable at shallower depths (below 1,300 °C, or at 9–13 GPa), whereas calcite–magnesite and alkali–calcite carbonate solid solutions are formed at deeper depths (Kiseeva et al. 2013). Upon thermal relaxation of a subducting slab, partial melting can occur in carbonated, fertile mantle at nearadiabatic temperatures (Thomson et al. 2016). The formed carbonatitic melts are unstable when percolating into the more reduced surrounding mantle, resulting in diamond formation through 'redox-freezing' (Rohrbach and Schmidt 2011). Both HP–HT experiments and natural inclusions in superdeep diamonds show evidence for the coexistence of diamond and carbonates or carbonatitic melts (Kiseeva et al. 2013) at oxygen fugacities of ΔIW+0.5 to +2.5 (Stagno 2019) at relatively shallow mantle pressures, declining to <ΔIW+1.2 at 14 GPa and 23 GPa, where carbonate may be reduced to form diamond (Thomson et al. 2016). Inspired by evidence that cooling of a CHO fluid might result in diamond precipitation in the lithosphere, new HP–HT experiments were carried out to test whether this mechanism also operates at sub-lithospheric depths. Cooling of silicate-rich and oxide-rich carbonatitic melts at 24–26 GPa (Si–Mg–Fe–Ca–Na–C–O2 system) (Spivak and Litvin 2019) leads to fractional crystallization of diamond followed by a sequence of assemblages of ferropericlase ±

bridgmanite ± other phases (Fig. 4), some of which have been observed in natural superdeep diamonds. However, as not all of these assemblages have been observed in natural samples (yet), and the ambient mantle has a higher temperature than the subducting slabs that serve as the sources of the oxidized carbonatitic and CO2 fluids, it remains to be determined if cooling and fractional crystallization leads to sub-lithospheric diamond formation in nature as it does in the laboratory.

CARBONATITIC METASOMATISM

Carbonatitic Mantle Metasomatism

The high mobility of carbonatitic melts, which have low viscosity and which wet silicate grain surfaces, implies that they would make effective metasomatic agents (Green and Wallace 1988). Experiments that examine carbonatitic melts interacting with lherzolite and harzburgite at pressures corresponding to shallow mantle depths (<90 km) produce wehrlitic assemblages (olivine + clinopyroxene). Reactions taking place have the following form:

1. orthopyroxene (enstatite) + carbonate/Ca–Mg carbonatitic melt → olivine (forsterite) + clinopyroxene (jadeite/diopside) + CO2 (fluid) (+ Ca-carbonatitic melt)

2. orthopyroxene (enstatite) + spinel + clinopyroxene + Na-carbonatitic melt → amphibole (pargasite) + olivine (forsterite) + CO2 (Yaxley et al. 1991)

The reaction of carbonatitic melt with orthopyroxene in depleted harzburgite or lherzolite likely produces a more Ca-rich carbonatitic melt plus wehrlite at decreasing pressures, whereas reaction of carbonatitic melt with fertile lherzolite results in a more Na-rich carbonatitic melt. Equilibrated wehrlites that form by carbonatitic metasomatism in the mantle are characterized by wellcrystallized olivine and clinopyroxene minerals, whereas the same reactions in unequilibrated mantle xenoliths instead contain fine-grained olivine and clinopyroxene, sometimes on rims of remnant orthopyroxene, with possible interstitial anhedral apatite on grain boundaries (Yaxley et al. 1991).

The interaction of a carbonatitic melt with the lithosphere results in a local fractionation of trace elements, enrichment in large ion lithophile elements (LILEs), LREEs, Ca, and P compared to high field-strength elements (HFSEs) such as Ti in the lithospheric rocks through which carbonatite moves, with the most pronounced enrichments in depleted harzburgite and dunite. Consequently, metasomatized xenoliths may display high Ca/Al, high Zr/Hf (above primitive mantle; >36), high La/Yb ratios, and Ti/Eu ratios below primitive mantle. Carbonatitic metasomatism can be distinguished from silicate metasomatism by the decoupling of LILEs and LREEs (which are enriched) from Ti (which is not) and by the lack of Fe–Al–Na enrichment in the rims of garnets and other minerals.

The conversion of orthopyroxene to olivine and clinopyroxene through the metasomatic process of carbonatitic melt–lithosphere interaction may not be important in the deeper lithosphere and asthenosphere, given the rarity of wehrlitic xenoliths and wehrlitic garnets in diamonds (Aulbach et al. 2020). However, other, more cryptic, evidence indicates that carbonatitic metasomatism occurs at depths in the deep lithosphere and below the lithosphere/asthenosphere boundary. Sinusoidal REE patterns in Cr-rich garnets can be created by carbonatitic metasomatism and are observed in harzburgitic and lherzolitic garnet inclusions in diamonds, providing support for carbonatitic metasomatism in the diamond stability field. Metasomatism in (sub-)lithospheric settings likely occurs in an open system via melt-channelized flow and a dissolution–precipitation process and, although we are unsure of the length-scales in natural deep systems, fast diamond growth appears to result from carbon-rich fluids transported along grain boundaries to diamond seeds. Included in these processes would be rapid growth of fibrous diamond and trapping of fluids that are out of chemical equilibrium with their host rocks.

Viscosity and Density Properties of Carbonatitic Melts

The first precise measurements of viscosity and density of carbonate melts at high P (2–5.5 GPa) and high T (530–1,500°C) were made using a falling sphere observed in situ with synchrotron X-rays (references in Jones et al. 2013). This reduced and extended the range of viscosity estimates from previous research (see Jones et al. 2013 and references therein) and established that viscosities of pure carbonate melts that have a range of chemical compositions lie between 1.5 x 10−2 to 5 x 10−3 Pa·s. These laboratory carbonate melts are reasonable analogues for mantlederived carbonatitic melts, confirming that the latter have the lowest viscosities of known terrestrial magmas (Jones et al. 2013). Basaltic melts, for example, have viscosities >2.5 Pa·s at pressures of 2–6 GPa. The extreme physical properties and inferred mobility of carbonatitic melts support their likely role in the flux of mantle carbon through the processes of melting and mantle metasomatism.

In natural systems, both in the crust and in the mantle, carbonatitic melts have been considered as ideal metasomatic agents, because their intrinsically low viscosities permit them to migrate along grain boundaries (Green and Wallace 1988). However, in natural rock systems, 'impure' carbonate melts (i.e., those containing silicate) may be less mobile than the predictions based on viscosities measured for pure carbonate melts, due to higher polymerization of the silicate-bearing melt. For example, experimental measurements of viscosities of carbonate–silicate and melilitic melts intermediate in composition between carbonatite and silicate liquids at pressures of 2.4–5.3 GPa and temperatures of 1,565– 2,155°C yield viscosities between 0.02 Pa·s and 0.08 Pa·s (Stagno et al. 2020). These values are low compared to common silicate melts, but one to two orders of magnitude higher than those of pure carbonate melts. Carbonatite melt may also be less mobile through silicate rocks where immiscibility separates that melt into co-existing silicate-rich and carbonate-rich melt phases; this is because silicate melt preferentially wets grain boundaries, preventing the carbonatite melt from migrating (Minarik 1998).

Prior to experimental measurements at much higher pressures, it was conjectured that carbonate melts would retain their low viscosity melt properties deep into the mantle. However, recent experiments above 40 GPa using carbonate glasses as analogues to carbonatitic melts reveal a surprising increase in viscosity by at least 3 orders of magnitude (>20 Pa·s) (Fig. 5); these viscosities are >1,000x higher than those of iron silicate liquids that could contain and move carbon in the lower mantle. Hence, the extremely low viscosity that characterizes carbonate melts in the crust and lithosphere may not extend down into the transition zone, and almost certainly not into the lower mantle. Instead, carbonate melts below the transition zone are likely to be much less mobile, with implications for the long-term storage and mobility of carbon in the deep Earth.

CARBONATITES AS TRACERS OF DEEP MANTLE PROCESSES

Both laboratory HP−HT experiments and observations of natural diamonds and mantle xenoliths confirm the stability of carbonate minerals and carbonatitic melts over a large depth range in the upper mantle. Constraining the relative contributions of carbonatites and diamond to the deep carbon cycle through time is not an easy task. Over the past ten years, major advances in our understanding of carbon on Earth have been made, especially through the DeepCarbon Observatory consortium. The uncertainty in the abundance of carbon on Earth has now been reduced, but still varies over a range of ~50–180 ppm for average upper mantle (Marty et al. 2016). The total amount of diamond brought to the Earth's surface in the past ~3 Gy is estimated at 7.35 billion carats (0.00147 Mt C) (Kimberley process statistics) and, thus, diamond is not a significant carrier of carbon from the mantle to the surface compared to, for example, mid-ocean ridges that can have a degassing rate of 13–30 Mt C y−1 (Fig. 5). It will take a multidisciplinary effort to constrain the diffuse degassing of CO2 from the continental lithosphere by the passage of magmas such as carbonatites, kimberlites, and CO2-bearing silicate melts by combining effusive gas measurements; geological reconstructions of the sizes of past rifts, basins, and fault systems; and more studies on wehrlitic xenoliths. Estimates from the proportion of rock affected by werhlitization suggest this process contributes between 1.4 ± 0.1 Mt CO2 y−1 and 70 ± 58 Mt CO2 y−1 of cryptic CO2 degassing per continental rift area (Aulbach et al. 2020).

Large uncertainties in the nature of deep carbon reservoirs, their temporal distributions, and the fluxes of carbon between them present challenges for future studies of Earth's carbon cycle. Nevertheless, carbonatite volcanism demonstrates connectivity and mobility between the mantle and the surface, coordinated on the scale of plate tectonics. We recognize the chemical fingerprint of ephemeral carbonatites in samples of lithosphere retrieved as xenoliths, and they are implicated in delivering carbon to sites of crystallization of some diamonds in which HDFs are trapped. It is currently poorly known how the fraction of C mobility and degassing from carbonatites compares to that from other CO2-rich melts, or how the fraction of stalled carbonatites compares to eruptive carbonatites, or the relative amounts of carbon stored in the sub-continental lithospheric mantle versus the sub-lithospheric mantle (Fig. 5). Nevertheless, carbonatites in the geological record attest to the importance for the carbon cycle to be tracked, because that is an indicator of this important class of CO2-rich magmatism. There are 609 known occurrences of carbonatite (Humphreys-Williams and Zahirovic 2021 this issue). These carbonatites have been emplaced since the Archean and appear more frequent since ~1.2 Ga, especially in the Mesozoic (as is the case for kimberlites) (Tappe et al. 2018; Humphreys-Williams and Zahirovic 2021 this issue). This temporal trend may be influenced by poor preservation of small-volume crustal carbonatite deposits. However, the increasing frequency of carbonatites through time could be linked to the following three factors: 1) the onset of subduction ~3 Ga, coinciding with the formation of eclogitic diamonds; 2) the development of possibly more oxidizing conditions in the upper mantle in the first billion years of Earth's history (Shirey et al. 2013 and references therein); 3) more abundant carbonates in subducting slabs since the Mesozoic. The more abundant presence of carbonates is caused by the emergence of abundant skeletal life as oceanic calcifiers and the formation of platform carbonates in the Mesozoic (Galvez and Pubellier 2019).

Figure 5 summarizes much of what we currently think we know: 1) there are low viscosity carbonatitic melts in the upper mantle, and higher viscosity in the lower mantle (>660 km); 2) there is production of Na-bearing carbonatitic melts from carbonated oceanic crust at 330–580 km; 3) there is a carbonatitic metasomatic signature in xenoliths and experiments; 4) there is the presence of carbonatitic signatures in mineral and fluid inclusions in lithospheric and sub-lithospheric diamonds (<660 km). All four of these points attest to the movement of carbon by carbonatitic melts, but this is restricted to the transition zone and the shallower mantle and has been limited to the past 3 Gy, mostly after 1.2 Ga.

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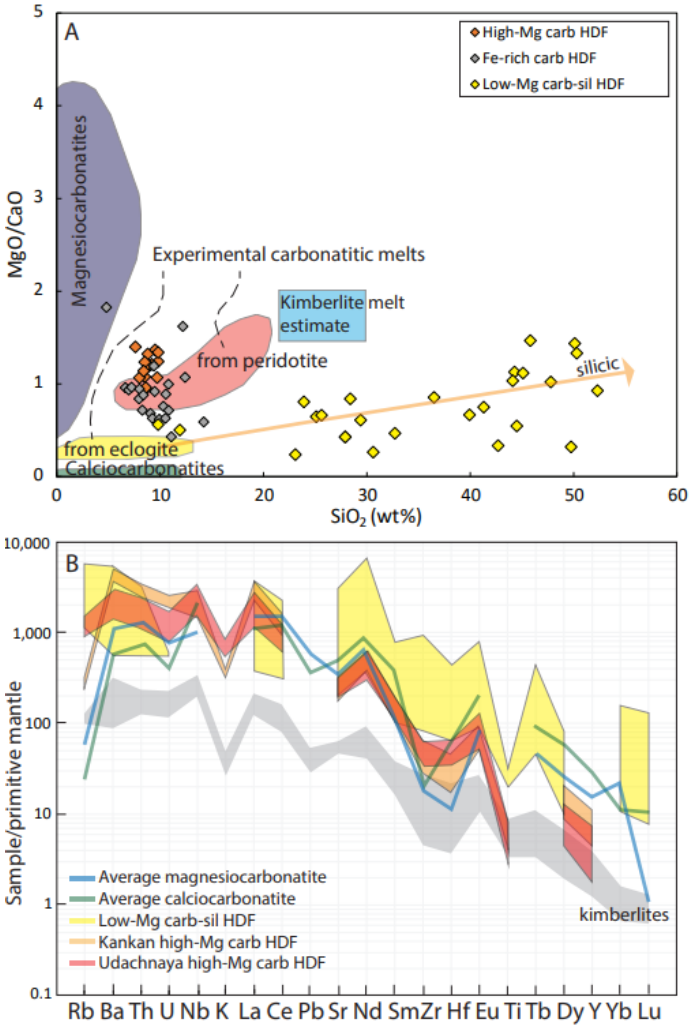

Figure 1: (A) Plot of MgO/CaO versus SiO2 diagram distinguishing low-Mg, high-Mg, Fe-rich carbonatitic highdensity fluid (HDF) and showing their similarities to experimental carbonatite melts. All have been normalized to 100% on a volatilefree basis. (B) Trace element patterns normalized to primitive mantle. Kankan carbonatite is from Guinea; Udachnaya carbonatite is from Russia. Abbreviations: Carb = carbonatitic; Sil = silicic. For data sources see http://elementsmagazine.org/supplements/.

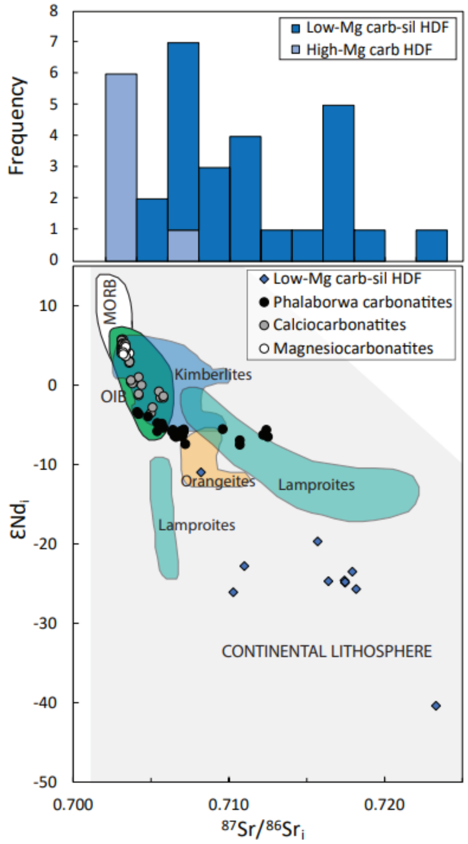

Figure 2: (lower) Plot of Nd versus Sr isotopic compositions (‘i’ refers to initial ratio) of mid-ocean-ridge basalts, ocean island basalts, kimberlites, orangeites, lamproites, carbonatite rocks, and high-density fluid (HDF) in diamonds, as calculated at the age of eruption. The Phalaborwa carbonatite is in South Africa. (upper) A frequency plot on the top shows Sr isotopic data for high-Mg and low-Mg carbonatitic highdensity fluid (some of which do not have Nd isotope data), highlighting the overlap in 87Sr/86Sr ratio of high-Mg carbonatitic high-density fluid with most carbonatite rocks. Abbreviations as per text and Figure 1A. For data sources see http:// elementsmagazine.org/ supplements/.

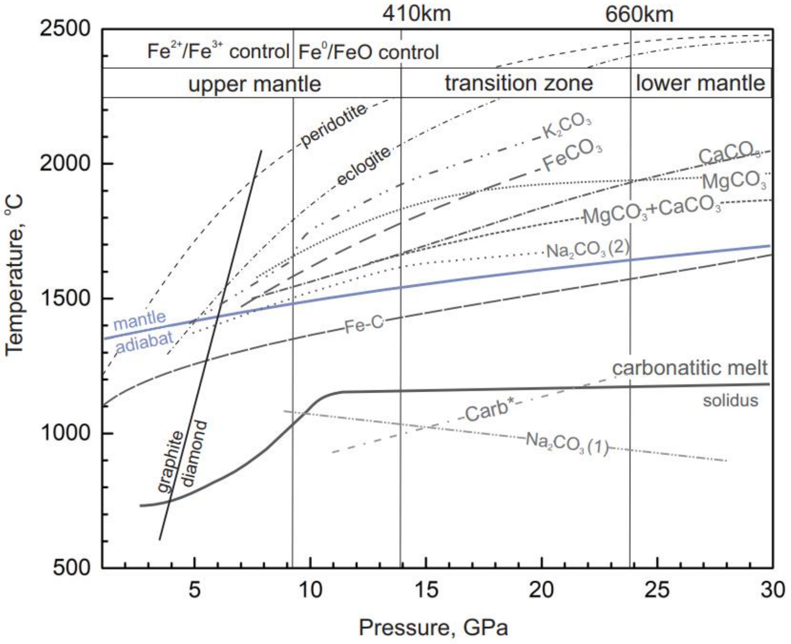

Figure 3: Diagram of melting and phase relations of carbonate and carbon-bearing systems. Grey lines: carbonate melting boundaries of MgCO3, FeCO3, CaCO3, Na2CO3, K2CO3; carbonate MgCO3–CaCO3 system; multicomponent carbonate system Carb* = MgCO3–CaCO3–FeCO3–Na2CO3; and eutectic temperature of the Fe–C system. Black dashed lines = peridotite and eclogite solidus. Black solid line = thermodynamic boundary of graphite/diamond. Blue solid line = mantle adiabat. For data sources see http://elementsmagazine.org/supplements/.

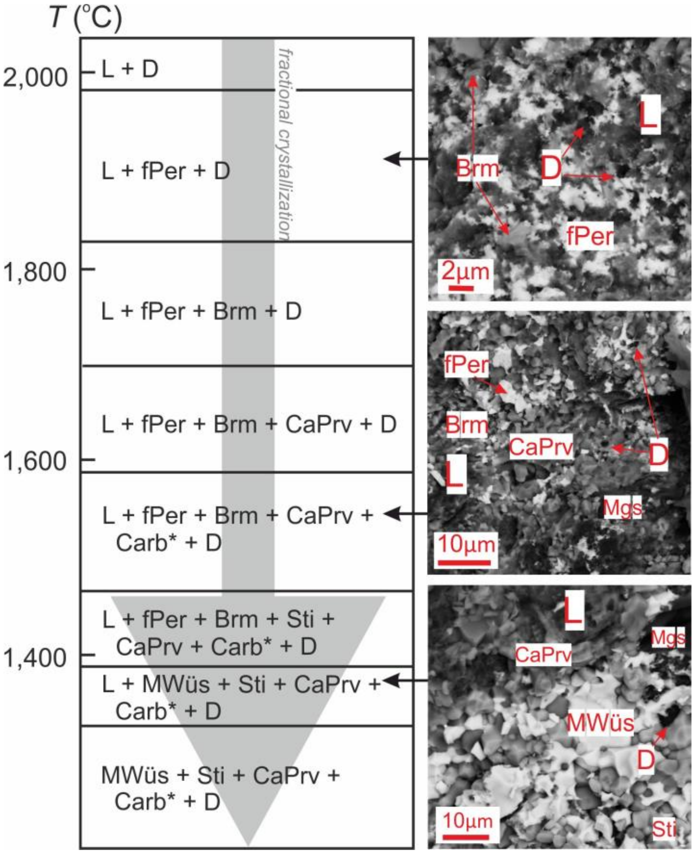

Figure 4: Schematic syngenesis diagram for formation of lower mantle diamonds and minerals during cooling of ‘melt pockets’ of silicate–oxide–carbonatite magmas of ultrabasic and basic assemblages. Experiments of syngenetic formation of diamonds and paragenetic minerals were carried out at 24–26 GPa. D = diamond (carbon), L = carbonate–silicate melt, fPer = ferropericlase, Bdm = bridgmanite, Sti = stishovite, Mgs = magnesite, MWüs = magnesiowüstite, CaPrv = Ca–perovskite, Carb* = Mg,Fe,Ca,Na–carbonates.

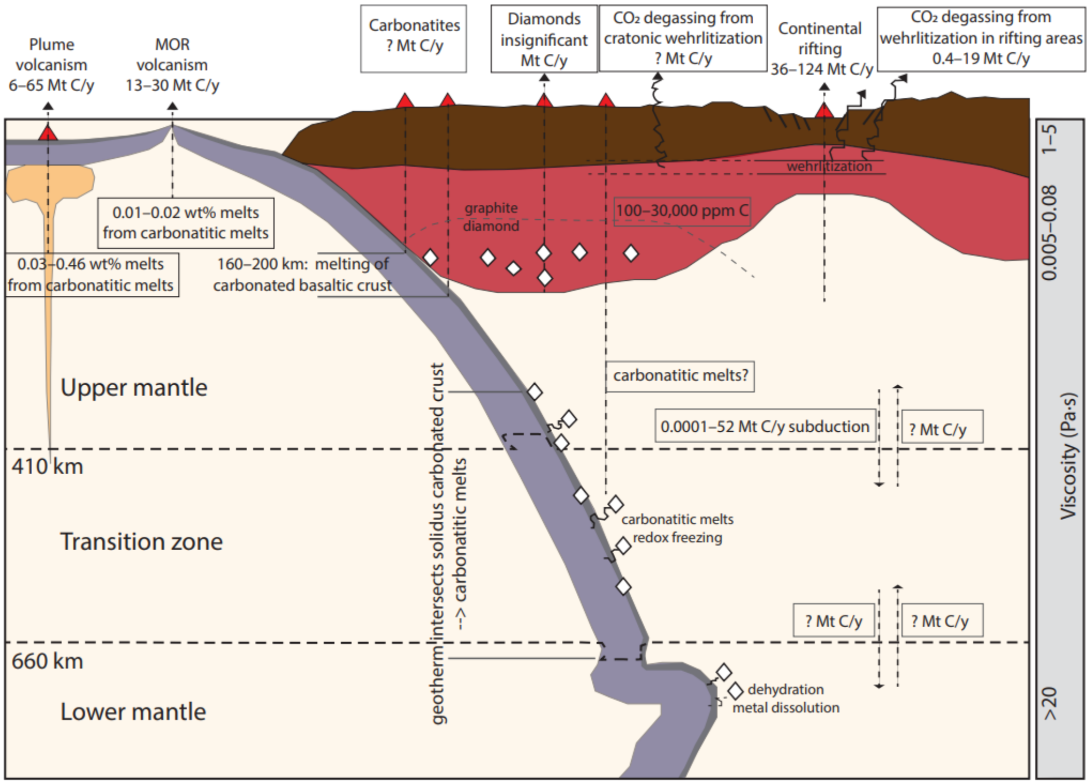

Figure 5: Schematic diagram showing the contributions of carbonate or carbonatite and diamond to the mobility of carbon between the mantle and the surface, representative of the last 200 My. Open diamond symbols = diamonds; MOR = mid-ocean ridge. For data sources see http://elementsmagazine.org/supplements/.