Super-reducing conditions in ancient and modern volcanic systems: sources and behaviour of carbon-rich fluids in the lithospheric mantle

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Abstract
Oxygen fugacity ($f_{O_2}$) is a key parameter of Earth’s mantle, because it controls the speciation of the fluids migrating at depth; a major question is whether the sublithospheric mantle is metal-saturated, keeping $f_{O_2}$ near the Iron-Wustite (IW) buffer reaction.

Cretaceous basaltic pyroclastic rocks on Mt. Carmel, Israel erupted in an intraplate environment with a thin, hot lithosphere. They contain abundant aggregates of hopper-shaped crystals of Ti-rich corundum, which have trapped melts with phenocryst assemblages ($Ti_2O_3$, SiC, TiC, silicides, native V) requiring extremely low $f_{O_2}$. These assemblages are interpreted to reflect interaction between basaltic melts and mantle-derived fluids dominated by CH$_4$ + H$_2$. Similar highly reduced assemblages are found associated with volcanism in a range of tectonic situations including subduction zones, major continental collisions, intraplate settings, craton margins and the cratons sampled by kimberlites. This distribution, and the worldwide similarity of $\delta^{13}C_i$ in mantle-derived SiC and associated diamonds, suggest a widespread process, involving similar sources and independent of tectonic setting. We suggest that the common factor is the ascent of abiotic (CH$_4$ + H$_2$) fluids from the sublithospheric mantle; this would imply that much of the mantle is metal-saturated, consistent with observations of metallic inclusions in sublithospheric diamonds (e.g. Smith et al. 2016). Such fluids, perhaps carried in rapidly ascending deep-seated magmas, could penetrate high up into a depleted cratonic root, establishing the observed trend of decreasing $f_{O_2}$ with depth (e.g. Yaxley et al. in Lithos 140:142–151, 2012). However, repeated metasomatism (associated with the intrusion of silicate melts) will raise the FeO content near the base of the craton over time, developing a carapace of oxidizing material that would prevent the rise of CH$_4$-rich fluids into higher levels of the subcontinental lithospheric mantle (SCLM). Oxidation of these fluids would release CO$_2$ and H$_2$O to drive metasomatism and low-degree melting both in the carapace and higher in the SCLM. This model can explain the genesis of cratonic diamonds from both reduced and oxidized fluids, the existence of SiC as inclusions in diamonds, and the abundance of SiC in some kimberlites. It should encourage further study of the fine fractions of heavy-mineral concentrates from all types of explosive volcanism.

Keywords Mantle redox · Moissanite (SiC) · Subcontinental lithospheric mantle · Mantle metasomatism · Abiotic methane

Introduction
Oxygen fugacity ($f_{O_2}$) is a key parameter of Earth’s mantle; it controls the speciation of fluids migrating at depth and therefore influences many processes, including diamond crystallization, volatile-bearing magmatism and metasomatism. The $f_{O_2}$ of the SCLM beneath cratons is heterogeneous and ranges from one order of magnitude above the quartz-fayalite-magnetite buffer ($\Delta$QFM+1) to at least $\Delta$QFM-3 (Ballhaus 1993; Frost and McCammon 2008; Stagno et al. 2013). Estimates of Fe$^{3+}$/Fe$^{2+}$ in depleted peridotites define an overall decrease of $f_{O_2}$ with increasing depth (Yaxley et al. 2012; Stachel and Luth 2015), but metasomatic overprints on this monotonic trend significantly increase the oxidation state.
of depleted cratonic peridotites because the latter have limited buffering capacity (Stachel and Luth 2015). However, some mineral assemblages (including moissanite (SiC) in kimerlites and diamonds) require much more reducing conditions, with fO2 at least as low as ΔIW-6 (Ballhaus 1993; Kadik 1997; Leung 1990; Wood et al. 1990; Yaxley et al. 2012). These observations imply the occurrence of localized volumes with significantly lower fO2 within the SCLM, and perhaps within the deeper mantle as well.

In this contribution, we discuss the wider significance of a remarkable example of super-reducing conditions in the uppermost mantle of an off-craton volcanic setting (Griffin et al. 2016a), which requires the introduction of carbon and hydrogen from the deeper mantle, at high fluid/rock ratios. We examine evidence for similar processes in other tectonic settings, and the implications for the transfer of carbon and hydrogen from the deeper mantle into the cratonic SCLM over time.

Super-reducing conditions in a Cretaceous volcanic system, Mount Carmel (Israel)

Upper Cretaceous (94–98 Ma, Turonian-Cenomanian) mafic to ultramafic pyroclastic rocks (vent breccias, tuffs) exposed on Mt. Carmel near Haifa, Israel represent a series of small explosive volcanoes that erupted on a shallow carbonate shelf (Sass 1980). Black pyroclastics occur in eruptive vents, while variegated pyroclastics occur as layers of various thickness interbedded with carbonates, indicating repeated explosive eruptions. Analyses of fine-grained, but possibly altered, la- pilli suggest that the magmas were tholeiitic to alkali picrites (Griffin et al. 2016a). The pyroclastic rocks carry mantle xenoliths (peridotites, pyroxenites) derived from <90 km depth (maximum P-T estimates of ca 1030 °C and 2.3 GPa), suggest- ing a thin lithosphere and a high thermal gradient (Esperanca and Garfunkel 1986; Mittlefehldt 1986; Kaminchik et al. 2014; Apter 2014; our unpublished data). They also contain a wide variety of xenocrysts: debris from garnet/spinel peridotites and pyroxenites, and megacrysts of clinopyroxene, ilmenite, zircon and corundum.

Over the last decade, the Shefa Yamim exploration project (www.shefayamim.com), focused on placer gem deposits, has recovered xenocrysts and megacrysts of moissanite (SiC) and corundum (sapphire, ruby and “Carmel Sapphire™”) from both the pyroclastic vents and the associated alluvial deposits. The “Carmel Sapphire” comprises aggregates (up to 4 cm) of hopper-skeletal crystals of Ti-rich (up to 4.5 at% Ti) corun- dum (Fig. 1), which are abundant in the pyroclastic deposits. Sampling procedures are described in the Appendix.

The melt pockets trapped in the corundum aggregates are confined by the euhedral to skeletal faces of corundum crys- tals, and the melts clearly have continued to precipitate corun- dum until each pocket was isolated from its neighbours. They can be divided into four types (Griffin et al. 2016a): Type S (silicate glass + oxides), Type A (alloys + carbides), Type N (nitrides + Ti borides) and Type DF (SiO2-free assemblages with fluorides). The different types appear to have been mu- tually immiscible at least during the late stages of corundum growth; they are found together in some melt pockets, or in separate pockets that may be linked in three dimensions (Fig. 1). They contain >100 different crystalline phases, many requiring very low fO2; more than half have not previously been reported as minerals, or are known only from meteorites (Xiong et al. 2017a, b).

In Type-S pockets the most common crystalline phases are tistartite (Ti2O3; Ti as Ti3+), a new phase designated TAZ ((Ti,Al,Zr)2O5; Ti as both Ti2+ and Ti3+) and Mg-Ti-Al spinel (Mg,Ti,Al)2O4 (Griffin et al. 2016a). These are embedded in a Ca-Al-Si oxide glass with a composition that varies within broad limits but includes high levels of Ti, Zr and light rare earth elements. Dmisteinbergite (the high-T metastable polymorph of anorthite) is a common quench phase. Its crystalliza- tion represents the reaction corundum + L = anorthite (i.e. the incongruent melting of anorthite), and constrains the pressure (>9.5 kb, <20 kb) and temperature (ca 1450 °C) of the system at the time of eruption (Goldsmith 1980). Grossite (CaAl2O4; see below) probably is not stable at pressures much higher than 1 GPa (Ottonello et al. 2013), providing a further constraint.

In Type-A pockets the two most abundant phases are TiC (khamrabaevite) and Fe2Si (guepette), but the pockets also contain a range of Fe-Ti-Si-P phases and rare moissanite (SiC) (Xiong et al. 2017a, b). In many cases the textural relationships suggest the unmixing or sequential crystallization of originally homogeneous alloy melts. The phase relationships (by comparison with experimental data on the Fe-Ti-Si sys- tem; Weitzer et al. 2008) suggest that these melts formed and evolved over a temperature range from ca 1500 to 1200 °C; the crystallization of SiC implies fO2 = ΔIW -6 (Ulmer et al. 1998).

Type-N pockets comprise mainly osbornite (TiN) with variable stoichiometry, accompanied by minor silicides, titaniu- m diboride and moissanite (Griffin et al. 2016a). They commonly show elongate forms with lobate boundaries; in some cases these form rectangular networks, suggesting that they were trapped in the internal cavities of skeletal Ti-rich corundum (Xiong et al. 2017b).

Type-DF pockets reflect the desilication of Type-A melts by the continued separation of immiscible Fe-silicide melts and SiC; they are represented mainly by angular grains of hibonite (CaAl4O7; see below) probably is not stable at pressures much higher than 1 GPa (Ottonello et al. 2013), providing a further constraint.
corundum form cores in some crystals of hibonite, evidence of the peritectic reaction corundum + liquid \( \rightarrow \) hibonite. The occurrence of native V requires \( f_{O_2} \) below \( \Delta IW = -10 \), equivalent to values in the early solar nebula, when it was dominated by hydrogen.

The sequence of mineral parageneses, the progressive lowering of \( f_{O_2} \) to nebular levels, and the P-T constraints suggest that the corundum and the low- \( f_{O_2} \) assemblages developed through interaction of mafic to ultramafic magmas with mantle-derived (CH\(_4\) + H\(_2\)) at high fluid/melt ratios (Griffin et al. 2016a; Xiong et al. 2017b), probably near the crust-mantle boundary in this area. The high initial temperatures (>1400 °C) derived from the mineral assemblages imply that these magmas were derived from great depths.

A schematic illustration of the proposed process is shown in Fig. 2; this model involves a magma chamber being flushed by a steady supply of CH\(_4\) ± H\(_2\), but other configurations are possible. The material described here comes from 8 different volcanoes, erupted over a time span of ~10 Myr and an area of ca 150 km\(^2\) (Segev et al. 2005), and provides snapshots of several similar magmatic systems sampled by eruption at different stages of their evolution. We have used these snapshots to reconstruct the evolution of a single synthesised system, from inception to eruption (Fig. 2). In this model, the early reaction of CH\(_4\) with the melt is inferred to have led to reduction of the melt via magmatic reactions such as

\[
Fe_2O_3(\text{melt}) + CH_4 \rightarrow 2FeO + CO_2 + 2H_2 \quad (1)
\]

Such redox reactions, at \( f_{O_2} \) near the QFM (quartz-fayalite-magnetite) buffer, may have been responsible for the precipitation of abundant, commonly vesicular, grains of wustite found as ejecta in the pyroclastics. The CO\(_2\) released by this redox process may have driven the precipitation of high-Mg calcite (crystallization \( T \approx 1400 \) °C; \( ^{87}\)Sr/\(^{86}\)Sr = 0.70334 ± 13, \( n = 35 \)), also found in the ejecta. With a continuing flux of CH\(_4\) this carbonate precipitation could continue to \( f_{O_2} \) as low as the enstatite-magnesite-olivine-carbon (EMOD/G) buffer. The further lowering of \( f_{O_2} \) to the IW buffer may be marked by the appearance of spherical balls of native Fe, Fe-oxide/silicate melts and Ti-oxide/silicate melts, interpreted as a suite of mutually immiscible melts. This immiscibility apparently removed most of the FeO from the system; none of the silicate phases in the trapped melts has significant contents of Fe (Griffin et al. 2016a).

The removal of the Fe-FeO buffer would allow \( f_{O_2} \) to decline to the levels (\( \Delta IW = -6 \)) where SiC could precipitate; our observations show that SiC coexisted with immiscible Fe-Ti silicide melts. This process would desilicate the residual melt (until now dominated by CaO-Al\(_2\)O\(_3\)-SiO\(_2\)), driving it into the liquidus field of corundum in the CAS system (Speyer 1996). The hopper-skeletal form of the corundum crystals in the aggregates (Fig. 1) implies Al\(_2\)O\(_3\)-supersaturation, leading to the rapid growth of corundum and the trapping of the melt pockets, described above. The continuing growth of the corundum led to strong concentration of the residual liquids, enriching them in Ti, Zr, REE and other incompatible elements, which ultimately crystallized a remarkable variety of phases (see partial list in Xiong et al. 2017b). The corundum itself has Ti contents up to 4.5 at%, increasing toward the pockets of trapped melts (especially Type-S pockets); this apparently reflects reduction of Ti\(^{4+}\) to Ti\(^{3+}\) (authors’ unpublished Electron Energy Loss Spectrometry (EELS) data, 2017). The desilication process apparently continued to very low \( a_{SiO_2}\), leading to precipitation of the assemblage hibonite (CaAl\(_{12}\)O\(_{19}\)) + grossite (CaAl\(_6\)O\(_{10}\)) + Mg-V-Al spinel + fluorite + native V, as \( f_{O_2} \) sank to \( \leq \Delta IW -10 \). Many of the larger corundum aggregates are cut by breccia veins with a matrix of...
carbon that is amorphous to transmission electron microscopy-Xray diffraction (TEM-XRD) and Raman spectroscopy (Fig. 1b); this material also occurs in parallel-sided, commonly vesicular, veinlets down to the micron scale, emphasising the important role of carbon in the evolution of these systems.

**Mount Carmel is not a unique occurrence**

The Mt. Carmel observations suggest that the mineral pair SiC + (commonly Ti-rich) corundum is a “smoking gun”, diagnostic of interaction between highly-reduced, C-rich fluids and mafic to ultramafic melts. Scattered literature reports indicate that this sort of interaction is more widespread than previously recognized.

Similar highly-reduced mineral assemblages (+ diamond) occur in the ophiolitic peridotite bodies of the Yarlong-Zangbo and Bangong-Nujuang suture zones (southern Tibet; Xu et al. 2009; Zhang et al. 2016; Griffin et al. 2016b; Xiong et al. 2017a) and the Polar Urals (Yang et al. 2015). In each of these cases, as at Mt. Carmel, most of the highly reduced phases, including nitrides, silicides and carbides, are found as inclusions in grains of Ti-rich corundum. The main difference between the ophiolitic and the Israeli volcanic occurrences is that some carbon occurs as diamond in the former (embedded in breccias of amorphous carbon; Yang et al. 2014; Zhang et al. 2016; Howell et al. 2015; Moe et al. 2017). Xiong et al. (2017b) therefore have suggested that the super-reduced assemblage in the ophiolitic occurrences crystallized in late-magmatic systems related to the rapid (<10 Ma) emplacement of the host peridotites from the Transition Zone to shallow depths, driven by slab rollback (McGowan et al. 2015; Griffin et al. 2016b).

Recognition of this reduced assemblage in volcanic systems has clarified that such assemblages do not require ultra-high-pressure (UHP) conditions, and has allowed a distinction between the UHP processes required for some of the Tibetan ophiolitic phases such as diamond, inverted calciferrite-structured spinel, and inverse ringwoodite (Satsukawa et al. 2015; Griffin et al. 2016b; Zhang et al. 2016) and the shallower processes discussed here, which are also observed in some ophiolitic occurrences. Similar “shallow” reducing processes probably are active today beneath the Kamchatka volcanic arc, where mafic pyroclastic volcanic rocks carry diamond, SiC and Ti-rich corundum (Karpov et al. 2014).

Peridotite xenoliths in basalts from the same area contain native metals and silicides, suggesting flushing of the shallow mantle wedge by H$_2$-rich fluids (Ishimaru et al. 2009).

The distribution of mantle-derived SiC (corundum) suggests that these processes operate beneath cratonic areas, as well as in subduction zones and off-craton intraplate settings.
such as Israel. SiC has been recognized as inclusions in diamonds from Siberia (Marshintsev 1990), the North China Craton (Fuxian kimberlite; Leung 1990), the Argyle lamproite in Australia (Jaques et al. 1986, 1989), Juina, Brazil (Hutchison 1997), the Sloan diatremes in North America and Monastery Mine in South Africa (Otter and Gurney 1989) and. High-Ti corundum also occurs as inclusions in diamonds in the latter two mines. SiC is also relatively common in heavy-mineral concentrates from Siberian kimberlites (Shiryaev et al. 2011; up to 1 wt%, V. Malkovets pers. comm. 2018). M. McCallum (pers. comm. 2017) has identified the diagnostic association of SiC + Ti-rich corundum in microdiamond residues from the Swartruggens kimberlite (South Africa). The Ti-corundum+SiC association is also reported from Devonian kimberlitic rocks in the Donets region on the edge of the Ukrainian shield (Tatarintsev et al. 1987) and in dundichrofrasive olivine-pyroxene xenoliths from the Karashofo shoshonite complex in Uzbekistan (Golovko and Kaminsky 2010; Kaminsky 2017). The most common inclusion in SiC from all localities examined by us is silicon metal, enclosing Fe-silicides and related phases (Shiryaev et al. 2011). These are high-temperature phases (1300–1500 °C; Weitzer et al. 2008), and their morphology suggests that they represent trapped volumes of the melts from which the SiC grew.

The streaming of low-/O₂ carbon-rich fluids from the upper mantle thus appears to accompany many types of volcanism, especially in tectonic situations that allow the rapid ascent and focussing of magmas (continental-collision zones, deep subduction zones, major transform faults). The transport of such fluids to shallower depths, possibly as components of deep-seated, low-volume magmas, is thus inferred to drive the local formation of low- /O₂ assemblages. If this mechanism is indeed widespread, then we can infer that similar processes must have affected the roots of cratons, as well as off-craton settings.

Volatiles and oxygen fugacity in the sublithospheric mantle

Possible sources of volatile components

The occurrence of SiC and other reduced phases in Kamchatka and in ophiolites from Tibet, the Urals, and Myanmar (Yang et al. 2015) suggests a relationship to subduction/exhumation processes, and there is considerable evidence that highly-reduced fluids can be produced by daywatering reactions in subducting slabs. For example, Song et al. (2009) have documented abundant CH₄ + C + H₂ fluid inclusions in the olivine of a fresh orogenic harzburgite from Northern China, interpreted as an exhumed mantle wedge. The C, He, Ne and Ar isotopes of these fluid inclusions are consistent with a shallow origin, probably from serpentinized peridotites and sediments of the subducting oceanic lithosphere. The coexistence of several types of fluids is consistent with geochemical modeling that predicts an expanded field of liquid immiscibility in the C-O-H system at high pressure, producing H₂O and C-rich gases (CH₄ + H₂, CH₄ + CO₂, and CO₂) at 1.5–2.5 GPa and 600–700 °C (Li 2016).

Brovarone et al. (2017) have documented the production of abiotic CH₄ through the reduction of subducted carbonates at 30–40 km depth, driven by breakdown of serpentine in the peridotitic part of the slab. In such cases, the generation of CH₄ can proceed until the fluids become C-saturated, leading to the precipitation of graphite and the generation of hydrogen. Experimental studies (Bali et al. 2014) have shown that under mantle conditions, H₂O and H₂ are immiscible; in this case the H₂ released by such reactions becomes a powerful reducing agent, even in the presence of water, and also can react with the precipitated graphite to produce more CH₄. The occurrence of diamond+SiC+CH₄+CO₂ inclusions in the garnet of Alpine UHP metasedimentary rocks (Janak et al. 2015) indicates that highly reducing conditions may exist in the crustal section of subducting slabs. The experimental generation of methane by reaction between FeO (in silicates), calcite and water at pressures of 5–11 GPa and temperatures of 500–1500 °C (Scott et al. 2004) also suggests that the abiotic production of methane may be widespread in deep subduction zones.

However, as noted above, the occurrence of the SiC ± corundum association is not specifically associated with subduction zones. For example, no subduction has occurred in the Levant area, where Mt. Carmel is situated, for at least 1 Gyr and there is no geophysical evidence for a relict slab beneath the area. In the Cretaceous this was an intraplate setting (Segev 2009), although trans-lithospheric faults related to the Arabia-Africa plate boundary (which became the Dead Sea Transform) represent potential pathways for mantle-derived magmas. There is also no clear relationship with subduction in the cratonic examples mentioned above. This suggests deeper, more pervasive sources for the CH₄ ± H₂ fluids, that are not confined to any distinct tectonic setting.

A major review by Etiope and Sherwood Lollar (2013) demonstrated that abiotic methane can be distinguished from biotic gas by the integrated use of carbon and hydrogen isotopes (including clumped isotopologues) and noble gas analysis, especially the presence of mantle-derived He. This type of high-temperature abiotic methane has been identified in volcanoes and related hot springs, both in arcs and at slow-spread oceanic ridges, suggesting that the leakage of abiotic CH₄ from the mantle is a widespread phenomenon.

The demonstration (Smith and Wang 2017) that Type IIb diamonds, which contain trace levels of boron (and inclusions of metal alloys and CH₄–H₂), are derived from the sublithospheric mantle or mantle transition zone (MTZ) is especially significant because B is an element that is
concentrated in the crust (Grew 2017), and its presence in the deep mantle is strong evidence for subduction recycling of crustal materials. It is interesting in this regard that the reducing fluids involved in the Mt. Carmel system carry boron, precipitated as TiB2 in the melt pockets (Griffin et al. 2016a), and that the Tibetan super-reduced paragenesis includes BN (Dobrzhinetskaya et al. 2014). Thus, while there is no evidence of subduction contemporaneous with the volcanism, mantle-derived fluids may still carry a subduction signature, perhaps inherited from slabs collected in the MTZ or the deep upper mantle (Palot et al. 2017).

**Oxygen fugacity in the sublithospheric mantle**

There appears to be a general consensus that a great deal of crustal carbon is recycled back into the mantle through subduction zones, because much of that carbon becomes stabilized in the slab as graphite, and is difficult to extract in melts (e.g., Galvez et al. 2013; Stagno et al. 2015; Duncan and Dasgupta 2017). The presence of large amounts of graphite will buffer O2 in the subducted ultramafic rocks (which have little inherent buffering capacity; Frost and McCammon 2008; Stachel and Luth 2015) at low levels, and this ultimately can modify the deep upper mantle (Palot et al. 2017), and suggest that the C and N both have ultimately been oxidized and reduced carbon-rich fluids (Palot et al. 2017), and suggest that the C and N both have ultimately been derived from shallow sources. These authors suggest that carbon and nitrogen in the MTZ, as a “slab graveyard”, could be dominated by recycled crustal materials.

The most significant control on the potential of the sublithospheric mantle to provide reduced fluids is the presence or absence of a metallic phase, specifically Fe-rich metal. In the presence of Fe6+, a C-O-H fluid will be dominated by CH4 + H2 with negligible CO2 and H2O (e.g., Matveev et al. 1997; Frost and McCammon 2008). Several experimental studies have produced evidence for the presence of Fe-rich metal in the deep mantle, though there is still disagreement about the depth at which this occurs. Frost et al. (2004) showed that the Fe3+/Fe of the perovskite phase is independent of fO2 but dependent on pressure, so that the lower mantle would have Fe3+/Fe of < 0.6. Since the Fe3+ is derived by disproportionation (FeO → Fe2O3 + Fe3+), they estimate that Fe alloys comprise ca 2 wt% of the lower mantle. Rohrbach et al. (2007) demonstrated that the same mechanism functions in the upper part of the sublithospheric (>250 km) mantle as majoritic garnet takes up Fe3+ with increasing pressure. Frost and McCammon (2008), modeling the experimental data and assuming a pyrolitic mantle, determined that Fe-metal saturation would be reached by 8 GPa; they also modified the earlier estimate of the free-metal content of the lower mantle to ca 1 wt%.

Frost and McCammon (2008) also suggested that diamonds might “exsolve” from Fe-Ni alloys (containing C) in the upper part of the lower mantle. This has been confirmed by the discovery of metallic inclusions (native Fe, Fe carbides) in lower-mantle diamonds (e.g. Hutchison 1997; Kaminsky and Wirth 2011; Hutchison et al. 2012; Kaminsky 2012, 2017). Several recent studies place the origin of many large Type II (both Ia and Ib) diamonds in the MTZ or lower mantle; they contain inclusions of metallic phases (e.g., cohenite + Fe-Ni alloy + sulfide), coexisting with CH4 and H2 (e.g. Smith et al. 2016; Smith and Wang 2017). These observations suggest that such diamonds crystalize and grow inside pockets of Fe-Ni-C-S metallic liquids, and that these liquids coexist with CH4 + H2 fluids (Smith et al. 2016). Shi et al. (2013) have demonstrated that at pressures <25 GPa, Fe melt in the mantle tends not to wet silicate surfaces, and would exist as isolated pockets; this would provide a growth environment for Type II diamonds. At higher pressures, the Fe melts develop into interconnected networks, allowing percolation.

Other recent studies have introduced greater complexity by showing that beyond methane and hydrogen, C-O-H fluids in reduced environments will develop a “rich variety” of heavier hydrocarbons, starting with C2H6 (Zhang and Duan 2009) and extending to acetic acid (C3H4O2) and acetate (Sverjensky et al. 2017). The fluid compositions will be pressure-dependent, dominated by methane in the uppermost mantle, and heavier hydrocarbons and molecular hydrogen at T > 1200 K (Lobanov et al. 2013). They will also be fO2-dependent; at fO2 near the IW buffer CH4, C2H6, C3H8 and C4H10 are the main carbon species (Sokol et al. 2017). This complicates the modeling of isotopic fractionations (see below), especially since such fluids, while ascending through the mantle, will become C-saturated as the fluid composition shifts to lighter hydrocarbons with higher H/C ratios (Lobanov et al. 2013), and diamond or carbides can be precipitated from a range of fluid compositions with (presumably) different isotopic fractionation factors. It is noteworthy that O’Reilly et al. (1990) identified a series of aliphatic heavy hydrocarbons in high-pressure fluid (mainly CO2) inclusions in spinel-peridotite xenoliths from alkali basalts in southeastern Australia. Measurements of He isotopes in these fluid inclusions showed an overabundance of He3+ relative to the atmosphere (R/Ra values of 7–10), consistent with a mantle derivation for the fluids (Porcelli et al. 1986).

Several lines of evidence therefore point to a generally low fO2, consistent with the coexistence of Fe-metal alloys/melts, in the MTZ and the lower mantle, and probably in at least the lower part of the upper mantle. However, estimates of the fO2 of isolated periclase inclusions in apparently lower-mantle diamonds span several orders of magnitude, and are generally more oxidizing than the IW buffer (Kaminsky 2017). This level of heterogeneity may suggest that these
particular diamonds formed in oxidizing environments (e.g., subducted slabs) isolated from the more reduced background environment represented by diamonds with metallic inclusions.

**Isotopic considerations**

The universal occurrence in SiC of silicon (Si) + Fe-silicide inclusions (Shiryaev et al. 2011) strongly suggests that the SiC grew from immiscible silicide melts, generated at very low $f_O_2$. Similarly, the ophiolitic diamonds contain inclusions of Ni-Mn-Co alloys, and their growth from immiscible metallic melts therefore is probable (Howell et al. 2015). The carbon in the SiC from Mt. Carmel is isotopically light ($\delta^{13}C = -25$ to $-33 \%e$; authors’ unpublished data), as is the SiC from ophiolitic occurrences and kimberlites worldwide ($\delta^{13}C = -18$ to $-35 \%e$, peak at $-27 \%e$; Trumbull et al. 2009). This range of values is also characteristic of the unusual diamonds from ophiolitic peridotites in Tibet and the Polar Urals ($\delta^{13}C = -18$ to $-29 \%e$; Yang et al. 2015; Howell et al. 2015; Moe et al. 2017). Similarly, $\delta^{13}C$ in the diamonds from the Kamchatka volcanics ranges from $-23$ to $-27 \%e$ (Karpov et al. 2014).

Most definitively lower-mantle sourced diamonds have a strongly restricted range of $\delta^{13}C$, close to $-5 \%e$ (Hutchison et al. 1999; Kaminsky et al. 2001). However, kimberlitic diamond populations, in particular those containing inclusions indicating derivation from the MTZ, or from kimberlites containing such diamonds, also have $\delta^{13}C$ in the range of $-15$ to $-25 \%e$ (Hutchison et al. 1999). Furthermore, populations from the Jericho (Slave Craton) and Guaniamo (Venezuela) kimberlites and the Dachine komatiites (French Guyana) extend to values as low as $-45 \%e$ (see review by Cartigny et al. 2014). Smith et al. (2016) reported variably light carbon, extending to $\delta^{13}C = -25 \%e$, in the CLIPPIR diamonds that contain metallic inclusions coexisting with CH$_4$ and H$_2$.

Chinn et al. (2017) reported that run-of-mine diamond populations from the Orapa kimberlite contain a high proportion of diamonds with $\delta^{13}C = -15$ to $-28 \%e$, with high [N] (to $>3000$ at. ppm) and positive $\delta^{15}N$, suggesting a “subduction” signature. The authors note that the present N-C isotopic database may be biased by the selection of diamonds with inclusions (to determine paragenesis) and the use of bulk-analysis techniques rather than in situ microanalysis, which reveals, for example, stones with $^{13}C$-depleted cores, and rims with “mantle” values.

The usual explanation for such isotopically light carbon is derivation from subducted organic carbon. The problem with this model is that it requires the complete removal of the isotopically heavy carbonate that comprises 80% of subducted carbon, before the organic material is extracted for the formation of diamonds or SiC (Cartigny et al. 2014). This model has been favoured in part because of the absence of observational or experimental data that would explain the large isotopic fractionations required to move $\delta^{13}C$ from the “mantle” range ($-2$ to $-8 \%e$) to such low values.

However, the observations presented here may offer insights into that problem, based on isotopic fractionation between a range of CH$_4$-rich fluids, metallic melts and phases such as SiC. We suggest that this type of mechanism could provide a widespread isotopic buffer in the sublithospheric mantle, and that the depletion of $\delta^{13}C$ is a signature of mantle-generated “abiotic” methane, representing one end-member in the carbon budget of the subcontinental lithosphere (see reviews by Etiope and Sherwood Lollar 2013; Douglas et al. 2017). The interpretation of N-isotope compositions may also need reconsideration; in the highly-reduced fluids/melts in the Mt. Carmel samples, the abundant nitrogen is present as nitrides, primarily TiN. This possibility will be tested by analysis of the N-isotope composition of the nitrides in the Mt. Carmel samples.

**Methane, diamonds and metasomatism in cratonic roots**

**Generalities**

One important aspect of sublithospheric diamonds is that although they have come from the deep asthenosphere, MTZ and/or lower mantle, they may have resided in the base of the SCLM until sampled by erupting kimberlites. This implies transport of deep-mantle, highly reduced fluids to the base of the SCLM, either by small (uneruptable) plumes or the continuous upwelling of the deeper mantle (Palot et al. 2017). This raises the question of how such fluids, coming from the reduced asthenosphere or deeper mantle, will interact with the SCLM, which is generally agreed to be more oxidized.

Estimates of the oxygen fugacity of the SCLM, as recorded by spinel/garnet peridotite xenoliths from kimberlites, show a general trend of decreasing $f_O_2$ with depth (Woodland and Koch 2003; Frost and McCammon 2008), from near the QFM buffer at shallow depth, to significantly lower values near the base. This reflects both the volume changes in the redox equilibria used to calculate $f_O_2$, and the progressive uptake of Fe$^{3+}$ in minerals such as garnet. A recalibration of the garnet oxythermobarometer (Stagno et al. 2013, 2017) has raised the $f_O_2$ estimates by about one order of magnitude, but the trend persists.

Yaxley et al. (2012), using garnet Fe$^{3+}$/[Fe] ratios measured by X-ray absorption near-edge spectroscopy (XANES), defined a gradient of $f_O_2$ in depleted harzburgite xenoliths from the lithosphere of the central Siberian Craton (Udachnaya kimberlite pipe); this trend intersects the IW buffer near the base of this lithosphere (Fig. 3). As in many lithospheric sections, the deeper part of this cratonic root has been refertilized, primarily by melt-related metasomatism (Fig. 3; Griffin et al. 1996) and is generally more oxidized than the shallower parts.
However, rare xenoliths of depleted harzburgites from the deeper parts of the cratonic root retain evidence of very low $f_{O_2}$ (Fig. 2; Woodland and Koch 2003).

These trends imply that an originally ultradepleted SCLM, exposed to an infiltrating reduced fluid, would develop such a gradient in $f_{O_2}$. Highly depleted dunites and harzburgites have very little buffering capacity; Luth and Stachel (2014) estimated that only 50 ppm of oxygen would be sufficient to move their recorded $f_{O_2}$ by four orders of magnitude. A methane-rich fluid ascending through the primordial SCLM would be progressively oxidised as it rose, with carbon being deposited as diamond, then as graphite at shallower levels. Barring later metasomatism, the harzburgitic SCLM would record the $f_{O_2}$ trend observed by Yaxley et al. (2012); Fig. 2.

Is there any evidence for this process? Stachel and Harris (2009) concluded that diamonds may have formed by both oxidation of methane and reduction of carbonates, while Jablon and Navon (2016) have argued that there is little evidence for the generation of diamonds from methane. However, fluid inclusions of methane have been described in diamonds from the Marange deposit in Zimbabwe (Smith et al. 2016), and from alluvial deposits in Siberia (Tomilenko et al. 1997). Other arguments for the growth of diamonds from methane-rich fluids have been based on the covariance of $\delta^{13}C$-N in single diamonds (Smit et al. 2016) and in a suite of coegenetic diamonds from a single xenolith (Thomassot et al. 2007). The latter study used 59 diamonds in a small xenolith from the Cullinan mine, and demonstrated correlations of [N], $\delta^{13}C$ and $\delta^{15}N$ that could best be explained by diamond crystallization from a methane-bearing fluid undergoing Rayleigh fractionation (oxidation) under mantle conditions (150 km depth, 1200 °C). This result was questioned by Stachel and Luth (2015) because Petts et al. (2015) determined a negative $\Delta N$ value for CH$_4$/diamond, rather than the positive value used by Thomassot et al. (2007). However, this argument may itself be flawed, because (as discussed above) reducing fluids coming out of the asthenosphere will contain not only methane, but a “rich variety” (Sverjensky et al. 2017) of heavier hydrocarbons, and a $\Delta N$ value for CH$_4$/diamond may not be relevant to the natural situation. In such fluids, a decrease in P and T can produce changes in pH that can precipitate diamond or graphite independently of redox processes (Sverjensky et al. 2017; Sokol et al. 2017. Stachel et al. (2017) modelled the variations in $\delta^{13}C$ of diamonds and concluded that fluid speciation, rather than silicate-buffered redox reactions, is the key factor controlling $\delta^{13}C$. Stressing the rarity of $\delta^{13}C$ depletion trends, they concluded that most diamonds have crystallized from CH$_4$- and CO$_2$-bearing water-rich fluids. Perhaps more importantly, they conclude that these fluids must have a narrow range of $X_{CO_2}$, which would imply a nearly constant initial $f_{O_2}$ for the fluid source, presumably the asthenospheric mantle.

In any case, the presence of SiC in diamonds and kimberlites (see above) requires the existence of $f_{O_2}$ conditions under which (CH$_4$ + H$_2$) is stable ($\Delta H - 6$ or less), and the oxidation of such fluids as they encounter more oxidizing conditions in the SCLM would promote the growth of diamond. Furthermore, the very low $f_{O_2}$ required for the formation of SiC strongly suggests the presence of H$_2$, which could be generated by the partial oxidation of CH$_4$ and the deposition of diamond or other forms of C (i.e. reactions of the form SiO$_2$ + 3CH$_4$ $\rightarrow$ SiC + C + 3H$_2$ + CO$_2$).
Fig. 4  Lithospheric sections (as in Fig. 3) beneath three cratonic areas with kimberlites of different ages. The sections illustrate the development over time of an Fe-rich, melt-metasomatised carapace at the base of the SCLM, which would act as a filter to capture and oxidize (CH$_4$ + H$_2$) rich fluids rising from the sublithospheric mantle. Estimates of the median Mg# of coexisting olivine, and of whole-rock Al$_2$O$_3$ content derived from the garnet data (see Fig. 3) reflect the extent of metasomatic refertilization at each depth. **Top:** Brockman kimberlite (ca 1800 Ma), Pilbara Craton, W. Australia. This is the oldest and most primitive SCLM section known; it has experienced minimal refertilization of the primary, highly depleted harzburgite. It would have very little buffering capacity and reduced fluids could penetrate high into it, producing an $f_O_2$ gradient like that seen in Fig. 3. **Middle:** Limpopo Belt kimberlites (ca 500 Ma), South Africa-Zimbabwe. Metasomatic refertilization has reduced the overall Mg# (and raised the Al content) of the whole section, but the most intense Fe-enrichment is concentrated in a 20-km thick zone at the base. In most kimberlites (illustrated here by data from Letlhakane and Orapa) there is a strong correlation of Fe enrichment with the distribution of eclogites; Type I eclogites, typically heavily metasomatised and commonly diamondiferous, are generally concentrated in the basal zone. This Fe-rich carapace would be a barrier to the passage of reduced fluids, and hence a source of CO$_2$ and H$_2$O for metasomatism, diamond formation and melt generation in this layer and above.

The refertilization of the keel from the base is obvious, but the changes in Fe content are moderate and mostly confined to a 10–15 km thick zone at the base. Mean compositions and P-T estimates are shown for two types of peridotite xenoliths. **Bottom:** N. Botswana kimberlites (90–100 Ma). Metasomatic refertilization has reduced the overall Mg# (and raised the Al content) of the whole section, but the most intense Fe-enrichment is concentrated in a 10–15 km thick zone at the base. Mean compositions and P-T estimates are shown for two types of peridotite xenoliths; Type I eclogites, typically heavily metasomatised and commonly diamondiferous, are generally concentrated in the basal zone. This Fe-rich carapace would be a barrier to the passage of reduced fluids, and hence a source of CO$_2$ and H$_2$O for metasomatism, diamond formation and melt generation in this layer and above.
A carapace model for the cratonic lithosphere

Several authors have suggested that kimberlites are derived from a relatively thin zone (a carapace) at the base of the cratonic SCLM, repeatedly re-fertilized by fluids from either the circulating mantle (e.g., Tappe et al. 2017) or plumes (e.g., Janney and Bell 2017; Woodhead et al. 2017). The plume model is attractive because it is consistent with the HIMU/OIB-like isotopic and trace-element characteristics of kimberlites worldwide (and the basalts of N. Israel; Stein and Hofmann 1992), as well as the occurrence of sublithospheric diamonds in kimberlites. In this type of model, kimberlites are generated as small melt fractions rich in CO₂ and H₂O, which are modified by interaction with the SCLM during their ascent (e.g., Stamm and Schmidt 2017; references therein).

Such a carapace is consistent with the generalized picture of SCLM composition built up by many years of lithospheric mapping, using xenoliths and xenocrysts from kimberlites worldwide (Figs. 3 and 4; Griffin et al. 1996, 1999a, 1999b). In a typical cratonic SCLM section, depleted harzburgites are concentrated in shallower parts of the SCLM, and show variable degrees of metasomatism, mostly by interaction with carbonatitic melts/fluids. The lower parts have been more strongly refertilized to produce lherzolites, mainly by interaction with silicate melts, raising their FeO contents and forming a highly irregular base to the SCLM (e.g., Begg et al. 2009; Griffin et al. 2013). In many such sections, this zone also hosts most of the eclogites (Fig. 4; Griffin et al. 1996, 1999a, 1999c, 2003, 2004; Griffin and O’Reilly 2007), further increasing the bulk Fe content and the Fe³⁺/[Fe] of the lower SCLM.

CH₄ + H₂ (±N, S) fluids ascending from a metal-saturated sublithospheric mantle into the base of the SCLM will be oxidized by reduction of Fe³⁺ in mantle minerals, producing CO₂ and H₂O, and CO at shallower depths (Frost and McCammon 2008; Zhang and Duan 2009) and/or carbonate melts (Stagno et al. 2013). The Mt. Carmel example demonstrates that at high fluid/rock ratios, the oxidizing capacity of the wall rocks can be exhausted, so that FeO will also be reduced, leading to the generation of Fe-silicate melts, SiC, nitrides and reduced carbon in localized highly-reduced domains.

The style and extent of these reactions will be controlled by the Fe³⁺/[Fe] of the rocks being infiltrated, and ultimately on their overall [Fe], representing their buffering capacity. The enrichment of the deep SCLM in Fe by the intrusion of silicate melts (including eclogites) would, over time, create a barrier to the infiltration of highly reduced fluids higher into the lithosphere (Fig. 4). It also would enhance the production of CO₂ and H₂O in this zone as the flux of CH₄ + H₂ (±N, S) fluids is oxidized, favouring the production of low-volume (carbonatitic to kimberlitic) melts through redox melting (Yaxley et al. 2017).

One consequence of such a model is that methane-grown diamonds may be more common in the shallower, harzburgitic portions of the SCLM, and that they may have grown early in the evolution of the SCLM, before the development of an Fe-rich carapace. Later in this evolution, oxidation of ascending sublithospheric CH₄ + H₂ fluids would provide a steady supply of CO₂ + H₂O for the generation of carbonatitic fluids, which could then be reduced to produce diamonds as they rise into the more depleted regions of the SCLM.

Other implications

Redox melting in the presence of abundant CH₄ ± H₂, rather than simply carbon, may also drive the desilication of wall rocks and melts in the deep lithosphere. This might, for example, explain the production of Al-rich lithologies such as corundum eclogites with negative Eu anomalies.

The recognition that CH₄ ± H₂ may accompany melts rising from a deeper, metal-saturated mantle also suggests an explanation for the zones of high conductivity that mark the tracks of some mantle-derived magmatic systems (from kimberlites to Bushvelds). The oxidation of CH₄ in rising fluids could propagate networks of amorphous carbon like those observed in the Mt. Carmel xenocrysts (Fig. 1). Even if later recrystallized to other forms, this carbon might provide the fine-scale connectivity of conductive material implied by the striking magnetotelluric images of crustal-scale fluid-transport systems, now becoming widely available (e.g., Selway et al. 2006; Selway 2014).

Conclusions

The Cretaceous volcanic rocks of Mt. Carmel can provide new insights into the role of low-/O₂, carbon-rich fluids in deep-seated magmatic systems. It seems apparent that delivery of such highly reduced COHN fluids from the deep Earth at least to the base of the lithosphere is a significant process, and commonly accompanies volcanism in a variety of tectonic environments. It is one aspect of what appears to be a worldwide phenomenon, and it may represent a continuous long-term leakage of carbon and hydrogen in reduced fluids derived from the deep upper mantle, the MTZ or the lower mantle below the MTZ. The worldwide similarity in the isotopic composition of SiC and of diamonds with metallic inclusions (both cratonic and ophiolitic) therefore suggests the operation of a reproducible process: the rise and reduction of abiotic methane, originally equilibrated with native metals in the sublithospheric mantle.

Where the lithosphere is thick, as in cratons, the oxidation of these fluids on contact with the SCLM can produce diamonds, and the CO₂ and H₂O released by oxidation may become agents of metasomatism and triggers for melting.
Where the lithospheric mantle is thin, as in Israel, graphite or even amorphous C may be deposited in highly reduced environments, while CO2 and H2O contribute to explosive volcanism. In major collision/subduction zones, such as Tibet and Kamchatka, reaction of such fluids with mafic magmas at intermediate depths, in rapidly evolving tectonic situations, may produce “unusual” diamonds (Howell et al. 2015; Moe et al. 2017) in localized reduced volumes within essentially transient environments.

A corollary of the apparent worldwide operation of these processes is that much of the sublithospheric upper mantle probably is indeed metal-saturated; otherwise it would present a barrier to the ascent of such reducing fluids to relatively shallow levels. In contrast, most cratonic mantle is underlain by a carapace of relatively fertile (Fe-rich) peridotite, commonly mixed with eclogites, which provides such a barrier to the infiltration of reduced fluids.

If the inferences presented here are correct, they may require revision of some current ideas about the carbon budget of the deep Earth and the SCLM, and of models that involve the direct introduction of CO2 and H2O into the lithosphere to produce metasomatism and melting. There is a great deal to be learned about these processes from a careful examination of heavy-mineral concentrates and mantle-derived xenoliths in explosive volcanic rocks, from kimberlites to volcanic arcs.

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Appendix: Sampling procedures

The Shefa Yamim exploration project (www.shefayamim.com) has sampled the Cretaceous pyroclastic centers on Mt. Carmel and adjacent areas, and minor and major drainages within the drainage basin of the Kishon River. Samples range in size from several kg to >1000 t. All samples were put through a static grizzly screen to remove pieces larger than 100 mm in diameter. Rock samples (black pyroclastics, consolidated) from the vents were coarsely crushed and then treated in the same way as alluvial samples. The material that passed the grizzly was washed in a scrubber that breaks up any clods. The <0.5 mm component is suspended in the wash water and pumped to settling ponds; fractions larger than 25 mm are used to backfill exploration pits. Samples in the +8 – 16 mm and + 16 – 24 mm size fractions are sorted by hand on a picking belt. The +0.5 – 8 mm component of the sample is washed and classified into 5 fractions: 0.5 – 0.7 mm, 0.7 – 1 mm, 1 – 2 mm, 2 – 4 mm, 4 – 6 mm, 6 – 8 mm. These fractions are transferred to a pulsating jig plant for gravity separation. Samples in the 2 mm – 8 mm size fractions are visually inspected after the jigging process and then sorted in the recovery laboratory. The three smallest size fractions are jigged separately. The heavy concentrate in the center of the jig pan is collected and dried; material on the outer part of the jig pan is discarded. The sorters in the laboratory have demonstrated their efficiency in identifying and recovering a wide range of mineral species, including garnet (pyrope), ilmenite, spinel, chrome-diopside, diamond, moissanite, sapphire, ruby, Carmel Sapphire and hibonite, as well as rutile and zircon.

Several samples of unprocessed heavy mineral concentrates provided by Shefa Yamim were hand-picked under a binocular microscope; a few rock samples also have been processed by selfFrag (electrostatic disaggregation) techniques, sieved and hand-picked after magnetic and heavy-liquid separation. Some larger xenocrysts, and mantle-derived xenoliths, were collected by hand from natural and artificial exposures in the vents and layered pyroclastics.

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