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A Geologic Si-O-C Pathway to Incorporate Carbon in Silicates

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ABSTRACT

Geologic and planetary processes are punctuated by sudden cataclysmic events, and planetary evolution is irrevocably changed by impacts and intense seismic and magmatic/volcanic activity. Such events often are associated with or generate high temperature, high pressure, and low oxygen fugacity. Their traces in the accessible geologic record are not pristine but altered by subsequent petrologic reactions. Evidence from the thermochemistry of synthetic materials, largely studied in a materials science context, in Si-O-C and M-Si-O-C-H systems under reducing conditions can be used to propose some possible rare but significant reactions, together called a geologic Si-O-C pathway, involving carbon-containing silicate melts, glasses, and amorphous materials. The substitution of carbon for oxygen in the first coordination shell of silicon provides a reducing local environment for the formation of metals, carbides, and silicides. Grains of these refractory compounds may persist long after the main carbon-containing silicate phase has transformed and disappeared. Such relict refractory materials may be markers of impact events and unusual volcanism. Anomalies in minor phases, trace elements, and textures in settings ranging from ultra-high pressure metamorphic rocks to impact craters to carbonado diamonds may be linked to the transient presence of carbon-rich silicate phases generated under reducing conditions from initially carbon-rich target rocks and/or impactors.

5.1. INTRODUCTION AND BACKGROUND

The chemical state of carbon coexisting with or dissolved in silicates at various conditions of temperature, pressure, and oxygen fugacity is critical to modeling the global carbon cycle and to understanding geologic and planetary processes. Under relatively oxidizing conditions, carbon can enter silicate melts, glasses, and crystals as carbonate (CO_3^{2-}) groups, and such equilibria have been studied extensively (Duncan et al., 2017; Kim et al., 2018; Kohn et al., 1991; Le Voyer et al., 2017; Mysen 2017). Molecular CO_2 can be confined in the pores and channels of open framework structures such as zeolites. Such porous phases and their surfaces, when containing

guest molecules, can undergo high-pressure phase transitions that are different from those in guest-free zeolites (Haines et al., 2010; Yong et al., 2018).

The substitution of carbon for silicon in tetrahedral sites of crystalline, glassy, and molten silicates has been a subject of speculation for many years. Computational and experimental studies have confirmed polymeric and tetrahedral framework (cristobalite-like) forms of carbon dioxide at pressures above 40 GPa (Oganov et al., 2008; Park et al., 2003; Seto et al., 2010). Carbonates containing tetrahedral CO_4^{2-} groups have also been proposed to exist above 80 GPa (Oganov et al., 2008). Although there is increasing evidence for such phases, their pressures of formation lie beyond the range of most petrologic processes. Nor can one directly address to what extent carbon can substitute for tetrahedral silicon in multicomponent silicates, given the large difference in Si-O and C-O tetrahedral bond lengths. One must then ask whether other more energetically affordable ways of incorporating carbon into silicates at lower pressure exist, especially

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under reducing conditions where CO_2 is destabilized and carbides can form.

The materials science and petrology communities have sought to put carbon into silica glass and silicates (Dasgupta et al., 2013; Fine & Stolper, 1986; Pantano et al., 1999). The direct incorporation of carbon into silica by high temperature reaction (including melting) is limited both by the low reactivity of silica and graphite in the solid state and by the carbothermic reduction of silica by graphite (Hutchinson et al., 1988) to form silicon carbide and carbon monoxide gas at temperatures above 1500 °C by the reaction



These difficulties have been circumvented by synthetic routes involving organosilicon compounds, whose controlled polymerization and pyrolysis at 500–1400 °C have led to a series of compositionally controlled “polymer-derived ceramics” or PDCs (Colombo et al., 2010; Mera et al. 2013) containing silicon, oxygen, and carbon (see Figure 5.1), as well as more complex systems containing those elements plus nitrogen, boron, hydrogen, and smaller amounts of other metals (Mera et al., 2013; Ionescu et al., 2013). Though amorphous by X-ray diffraction, PDCs show complex interpenetrating

nanostructures of silica-rich and carbon-rich domains. The domains are thin, fractal, and intergrown. Within the silica-rich domains, carbon substitutes not for silicon but for oxygen, leading to “mixed tetrahedra” ($\text{SiC}_n\text{O}_{4-n}$) with silicon at the center and zero to four carbon atoms in the first coordination shell, as documented by extensive spectroscopic studies, especially by nuclear magnetic resonance techniques (Mera et al., 2013; Widgeon et al., 2010) (see Figure 5.1). The carbon in the silica-rich domains is not uniformly distributed but tends to be enriched near their interfaces with the carbon-rich domains.

PDCs persist to about 1500 °C, until the carbothermic reduction reaction (Equation 5.1) sets in (Hutchison et al., 1988). It was initially assumed that the PDCs were thermodynamically metastable and their lack of decomposition at high temperature below that of carbothermic reduction was a result of kinetic hindrance. However, calorimetric studies of their enthalpies of formation showed that many PDC compositions are stable in enthalpy relative to a mixture of crystalline SiO_2 , SiC , and C (Mera et al., 2013; Varga et al., 2007). Since the entropies of the disordered and nanostructured PDCs are almost certainly higher than those of a mixture of crystalline components, the negative enthalpies of formation coupled with positive entropies of formation make them thermodynamically stable, having lower Gibbs free energy of formation than an isochemical

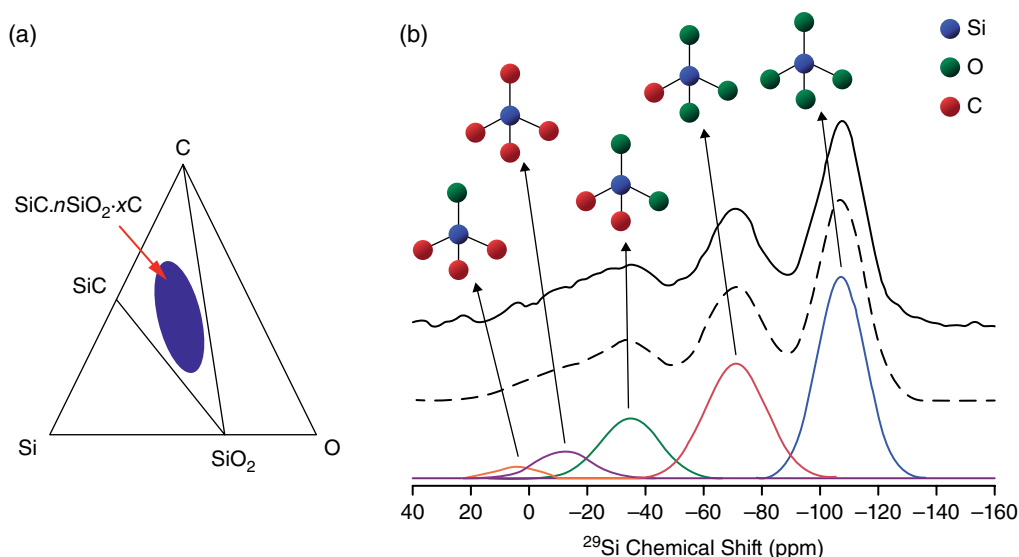


Figure 5.1 (a) Approximate composition range (mole fraction basis) over which polymer-derived ceramic (PDC) phases form in the Si-O-C system. (b) ^{29}Si MAS NMR spectra of a polysiloxane-derived SiOC PDC of composition $\text{SiO}_{1.5}\text{C}_{0.68}$ pyrolyzed at 1100 °C in argon. The experimental spectrum is shown by the solid bold curve on top, followed by the simulated spectrum (dashed curve), and the individual simulated components (bottom, solid curves). Peaks from right to left correspond to SiO_4 , SiO_3C , SiO_2C_2 , SiC_4 , and SiOC_3 groups, as modeled by deconvolutions, with the SiOC_3 and SiC_4 groups not always clearly separated in the experimental data (Mera et al., 2013). This figure illustrates the power of NMR to distinguish mixed-bond tetrahedra. See electronic version for color representation of the figures in this book.

mixture of crystalline components. This observation led us to speculate that analogous carbon-containing glassy, liquid, or crystalline phases, with carbon substituting for oxygen rather than for silicon, might form under reducing conditions in the crust and mantle. Reducing conditions are obviously required to minimize the formation of CO_2 or carbonates (Kadik et al., 2004; Sen et al., 2013). Very high pressure is not required, but moderate pressure would disfavor the carbothermic reduction reaction, which produces a gas phase and would thus extend the stability field of the silicon oxycarbide phases to higher temperatures. Later diamond cell and multianvil experiments in the Navrotsky group on mixtures of silica glass, silicon carbide, and graphite were inconclusive because of very slow reactions, even at temperatures of 1500–2000 °C and pressures of 5–10 GPa and therefore were not published. Thus, it is not clear at present how pressure affects the stability and decomposition of PDCs or whether, if gas evolution and crystallization are suppressed, they can melt to produce carbon-containing silicate liquids with mixed-bond tetrahedra. The discussion below suggests that PDC-like solids can be produced in several ways: by condensation from a vapor, by cooling of a multicomponent supercritical fluid from very high temperature and pressure, or from a silicate melt at low oxygen fugacity and moderate temperature and pressure.

Motivated by the observed thermodynamic stability of PDCs, we conclude that the polymer route was a kinetic and mechanistic convenience, allowing a synthetic pathway to a stable product. Thus, the product should be attainable by other simpler means not involving organometallic polymer precursors. Laser ablation of a silica glass target in an acetylene atmosphere (Tavakoli et al., 2015) produced a powder that had many of the attributes of the PDC materials, though it was fine grained and contained more hydrogen. It contained mixed-bond $\text{Si}_n\text{O}_{4-n}$ tetrahedra and had comparable energetic stability to PDCs of similar composition. Its method of synthesis, rapid formation of a plume of vapor and particles followed by rapid collection on a cold substrate, has some similarity to a geologic impact process, and the observations made us think of the role of Si-O-C melts, glasses, and amorphous solids in impact phenomena.

It is possible that C can substitute for O in amorphous PDC-like materials other than pure silica, with implications for reduced silicate melts in the Earth's mantle (Sen et al., 2013). For example, carbon substitutes for oxygen in lithium silicate systems of less than full polymerization, extending the possible range of compositions for PDC-like materials to be more geologically relevant in terms of Q-speciation (Qn (n = 0 to 4) being the average number of bridging oxygens in a silicate tetrahedron) (Sen et al., 2013). Later studies synthesized PDCs with Mg and Mg+Ca (Ionescu et al., 2018). Although phase separation and crystallization were complications,

Table 5.1 Crystalline phases formed upon annealing of metal-containing Si-O-C polymer-derived ceramics (Ionescu et al., 2013).

Metal Added	Phases Observed
Zr	ZrSiO_4
Hf	HfSiO_4
Mn	MnSiO_3
Lu	Lu_2O_3 , $\text{Lu}_2\text{Si}_2\text{O}_7$
Sn	Sn
Fe	Fe_3Si , Fe_3Si_3 + SiC
V	V_8C_7

substitution of C for O was indeed seen, including in the more depolymerized glass phase of lower silica content that coexists with almost pure silica in the carbon-free MgO-CaO-SiO₂ system. The energetic stability of these alkaline earth PDCs, determined by calorimetry, is generally comparable to that of other Si-O-C materials studied earlier. In addition, some of these compositions appear bioactive toward hydroxyapatite formation, while others are not. This may have relevance to medical implants and perhaps even to the origin of life and its evolution.

We are currently working on laser ablation studies on a sintered crystalline forsterite (Mg_2SiO_4) pellet. The product of ablation in acetylene is black, amorphous to XRD, and appears to be close to forsterite in composition. Preliminary results suggest some carbon incorporation.

In another set of studies, a number of different metals were incorporated into the polymer, which was then pyrolyzed; initial metal incorporation in the PDC was followed at higher temperature by crystallization of secondary phases (Ionescu et al., 2013). The results are given in Table 5.1. Metals, oxides, or silicides are crystallized, controlled by thermodynamic stability at the C-CO equilibrium. Thus, the metals whose oxides are stable at the C-CO equilibrium (Zr, Hf, Mn, Lu) form oxides that react further with the silica component to form silicates, Sn remains as elemental tin, Fe forms silicides, and V forms carbides. The formation of ternary oxides and the potential competition between carbide and silicide formation appear to be controlled by the phase(s) of lowest free energy, suggesting equilibrium is attained relatively rapidly.

5.2. HYPOTHESIS: THE GEOLOGIC SI-O-C PATHWAY

Impacts and some deep-seated magmatic processes produce local very high temperatures and locally reducing conditions that can generate transient silica-rich vapors, supercritical fluids, or melts containing all the constituents of the host rocks, their associated fluids, and the impactor. These short-lived products can contain significant carbon substituting for oxygen and may be

precursors to geologic Si-O-C materials whose carbon is available for further chemical reaction, without the need to equilibrate with an external carbon-bearing fluid. Such geologic Si-O-C materials may be similar to materials made in the laboratory by PDC and laser ablation routes that contain silica-rich and carbon-rich nanodomains. The geologic Si-O-C materials can precipitate small amounts of uncommon oxides, metals, carbides, carbon, silicon, and silicides. These widely disseminated crystalline grains reflect thermodynamic equilibrium under the pressure, temperature, and low oxygen fugacity conditions of the initial event. High pressure is not required for their formation, and the oxygen fugacity is, to a first approximation, that of the C-CO equilibrium. The silica-rich nanodomains can undergo relatively rapid alteration, and their metamorphosed products may not be readily identifiable, but the refractory carbon, metal, carbide, and silicide grains may be able to survive cycles of alteration through geologic time (analogous to refractory zircon grains), sometimes preserving morphological evidence of having been molten or crystallizing from a vapor, melt, or glass. These refractory grains of highly reduced phases provide strong evidence for the initial cataclysmic impact or magmatic event. For brevity, the sequence of events described above is referred to as the geologic Si-O-C pathway.

5.2.1. Geologic Evidence for the Si-O-C Pathway

The geologic Si-O-C pathway provides a mechanism for formation and evolution of carbon-containing silicates under internally controlled low oxygen fugacity and having an internal source of carbon, without the need for (though not precluding) ultra-high-pressure conditions. Ahead, we briefly discuss some petrologic observations and geologic scenarios that may be consistent with evolution along the geologic Si-O-C pathway.

Impact events are obvious candidates. Giant impacts, relatively common in the late stages of planetary accretion, can produce significant melting and/or vaporization of large fractions of a planet (Cuk et al., 2016). The condensation of silica-rich (supercritical) vapor can produce a melt rich not just in rock-forming mineral components but also in metals and carbon coming from the impactor (e.g., a metal-rich bolide or a planetary impactor with a metallic core) and from the initially vaporized carbonates, fluids, and organic matter in the host rocks. The initial ultra-high temperatures (thousands of degrees) and pressures (tens to hundreds of GPa) dissipate rapidly, but the extensive melt formed, termed a *magma ocean* if it covers much or all of the planet's surface, initially will contain a relatively homogeneous distribution of all the above components. As it cools, such a melt may transform into a glass that contains carbon-rich and

silicate-rich domains, precipitating metals, carbides, and silicides, maintaining low oxygen fugacity at least locally, and evolving along the geologic Si-O-C pathway suggested above. Alternatively, the supercritical fluid or vapor may condense directly to an amorphous material (glass), which then undergoes similar evolution.

Though we have no direct petrologic evidence of the likely largest impact on Earth, namely the Moon-forming event, there is evidence to support the geologic Si-O-C pathway from a number of smaller (though still large and cataclysmic) impact events. The Sudbury structure in Ontario, Canada, is the third-largest known impact crater on Earth. Both the commercial interest in nickel and the accessibility of the crater have allowed extensive field, petrologic, and geochemical studies (Dietz, 1964; Grieve et al., 1991, 2010; Lightfoot, 2017; Ubide et al., 2017). Of particular interest is the likelihood that the initial impact initiated volcanic activity involving melting of a large amount of crust over a relatively long time, as well as interaction of the volcanic activity with seawater; see Ubide et al. (2017) for a review. These authors also argue that impact-triggered volcanism may be a more general planetary phenomenon (and better preserved) on Mercury, Venus, and Mars than on Earth.

From the present point of view, we seek evidence of carbon incorporation in the initial impact melt and in subsequent volcanic melts. The impact basin fill at Sudbury, referred to as the Onaping formation, is a complex 1.4–1.6 km thick brecciated *mélange* consisting of several distinct members, ranging in color from black (carbon-rich) to green (the color suggesting high ferrous ion concentration consistent with reducing conditions) (Grieve et al., 2010). Each member contains varying amounts of vitric clasts (suggested to be glass or to have come from glass), lithic clasts and shards (showing crystallinity and complex textures), and cross-cutting dikes. The average silica content is about 63 wt%. Grieve et al. (2010) argue for water being essential to the postimpact history to produce the observed lithologies and textures, but that issue is tangential to the major hypothesis in the present work. The Onaping formation contains variable carbon content, ranging from 0.5 to 6 wt% in different members, but some carbon appears everywhere. The carbon is isotopically light, and its concentration correlates with that of iridium. Various biogenic, sedimentary, hydrothermal, and other sources for the carbon have been proposed, but none is fully convincing.

The geologic Si-O-C pathway may explain some of the above observations. The initial carbon could have come from the bolide, the host rocks, although carbon-rich sediments are absent from the target sequence, or from some combination thereof. Regardless of the carbon source, the high temperature and reducing conditions produced by the impact, coupled with the silica-rich host rocks,

could have produced geologic Si-O-C materials, perhaps initially in the molten state. Their subsequent evolution through the nanostructured ceramic stage could have produced the observed vitric silica-rich fragments and graphite. The ubiquitous but varying distribution of this carbon, not well correlated with other geochemical, petrologic, or textural indicators, suggests its presence in the initial melt. Its variation may reflect locally different subsequent histories, perhaps related to volcanism and reactions with water. The reported presence of lonsdaleite, impact diamonds, and fullerenes (Lightfoot, 2017) also needs to be considered. These could form from the carbon initially in the geologic Si-O-C melt or glass.

The synthesis of diamond-like carbon outside the diamond stability field has been well documented in the materials field, e.g., by chemical vapor deposition or by the action of chlorine gas on silicon carbide at atmospheric pressure and temperatures as low as 1000 °C (Gogotsi et al., 2001). Thus, the presence of diamond-like phases is not necessarily an indicator of high pressure, and their absence is not a reliable indicator of low pressure, since diamond may transform or decompose after initial formation. An unanswered question is whether, and under what conditions, diamond, rather than graphite, can crystallize from the Si-O-C melt, vapor, or nanoceramic. If nanodiamond forms, it may be further stabilized with respect to graphite by surface energy effects. This topic needs further experimental investigation, but the tentative conclusion is that one cannot exclude the formation of metastable diamond at low pressure by the geologic Si-O-C pathway.

Libyan Desert glass is widely distributed over an area of approximately 4000 km². Its origin is generally attributed to a 29 Ma impact event, but no source crater has been definitely identified. Pratesi et al. (2002), using transmission electron microscopy, identified spherules arising from silicate-silicate glass immiscibility. They also found 5–50 nm thick graphite ribbons polygonalized into closed structures up to 200 nm in diameter. Such textures are quite similar to those in annealed PDCs in the Mg-Ca-Si-O-C system (Ionescu et al., 2018). Thus, these observations are consistent with a process involving impact into silica-rich sediments, formation of a geologic Si-O-C melt, cooling to a geologic Si-O-C glass or nanoceramic, and phase separation into two silicate glass phases plus a carbon-rich phase. If the Libyan Desert glass is sufficiently unaltered, one might find the presence of mixed SiC_nO_{4-n} tetrahedra by NMR or other techniques.

Widely distributed, altered “impact spherules” have been reported to be potentially associated with the 2.02 Ga Vredefort impact structure in South Africa (Kamo et al., 1996). They are also found in a dolomitic layer in the Ketilidian orogeny in Greenland (Chadwick et al.,

2001), in which spherules contain concentrations of carbonaceous material, and in the Zaonega Formation in Karelia, which contains spherules with bituminous material (Huber et al., 2014). A nanodiamond-rich layer spanning three continents is suggested to be associated with an impact contemporaneous with the start of the Younger Dryas climate fluctuation and extinction event about 12,800 years ago (Kinzie et al., 2014). This layer also contains carbon spherules that, however, could be fire ash. Their very recent age and possibly relatively unaltered condition make the silicate spherules, carbon spherules, and nanodiamonds a very promising assemblage for further study and possible detection of mixed-bond tetrahedra suggested by the geologic Si-O-C pathway.

Carbonado is a rare and enigmatic form of diamond-like carbon. As summarized by Haggerty (2014), it is 3.8 Ga old, polycrystalline, and porous but strongly bonded and super hard. It contains silicate and other mineral inclusions consistent with crustal rocks and their alteration products, and inclusions of metals, SiC, FeC, TiN, and new ternary Cu, Ti nitrides. The latter group of inclusions is indicative of strongly reducing conditions and possibly very high temperature. Textural evidence suggests that some of the carbonado diamond surfaces may have been molten, again suggesting very high temperatures and pressures. However, the porosity argues against a high-pressure origin. Considering the contradictions in all conventional models of terrestrial carbonado formation, Haggerty turned to possible extraterrestrial origin. He suggested that carbonado was delivered to the early Earth from sources such as carbon-rich exoplanets or the interiors of large gaseous planets.

Does the geologic Si-O-C pathway remove some of the inherent contradictions in proposed terrestrial origins for carbonado? Is an impact origin that generates carbonado on Earth rather than bringing it previously formed in an extraterrestrial impactor possible? Although each carbonado is massive compared to other diamonds, the total amount of carbon tied up in them is small because they are rare. Thus, their rarity may reflect the need of the bolide to strike a local carbon-rich lithology. The reduced carbide and silicide phases are consistent with phase equilibria controlled by the C-CO equilibrium at 1000–1500 °C, and indeed mirror those seen in the PDCs. The porosity of 10% or more may represent the removal by alteration of the silica-rich phase in the nanoceramic, leaving some behind as silicate mineral inclusions. In PDCs, the interfaces between silica and carbon domains concentrate the mixed bonds, and their removal may indeed lead to surface smoothing and reconstruction of the remaining carbon, without actual melting. PDCs also readily incorporate nitrogen and hydrogen (Colombo et al., 2010), providing a precursor for their incorporation

into carbonado. Studies of the annealing and weathering of the PDC analogues may produce unique textures and size distributions; whether these suggest carbonado is not known. Thus, the geologic Si-O-C pathway needs further experimental study in the context of carbonado formation, as it may provide a tenable mechanism of formation of such carbon nanocomposites at relatively low temperature and pressure. Furthermore, the geologic Si-O-C pathway may provide a mechanism for carbonado formation in carbon-rich planets as well.

A final example is the occurrence of silicon carbide (moissanite) containing inclusions of silicon and complex silicide phases related to FeSi_2Ti , Si_2TiV_3 , and FeSi_2 (Dobrzhinetskaya et al., 2018). The SiC is hosted in a pyroclastic tuff derived from alkali basalt formations in northern Israel. The latter may be related to hot spot volcanism (Eppelbaum et al., 2004). In preparation of hand specimens for study by Raman spectroscopy and transmission electron microscopy by Dobrzhinetskaya et al. (2018), extreme care was taken to avoid contamination, and the moissanite and its inclusions are considered to be native to the tuff. It is striking that the iron and vanadium silicides, though more complex in composition than those in simple binary systems, are very similar to those found to crystallize from iron- and vanadium-doped polymer-derived ceramics (see Table 5.1). The silicide inclusions often show a spherical morphology consistent with crystallization from a melt. The authors consider melting in silicon carbide–metal silicide systems and conclude that the molten alloy droplets could have formed at temperatures similar to those of basalt melting. It is generally assumed that the SiC needed to be transported as xenocrysts from the upper mantle or transition zone where they formed under extremely reducing high-pressure conditions to the shallower depth of active volcanism. However, Dobrzhinetskaya et al. (2018) suggest that “the studied SiC formed as a result of an interaction of a small volume of reducing fluids and crustal materials (SiO_2) possibly available from the walls of the alkaline basalt reservoir.” The proposed geologic Si-O-C pathway can take such a reducing fluid, or a graphitic or organic carbon source, and by dissolving carbon in the silicate melt (basalt) retain reducing conditions through the evolution of carbon-containing melt to glass to nanophase ceramic and the subsequent precipitation of silicon carbide and its associated carbide and silicide inclusions. Neither melting of the carbide or silicide nor very high pressure is required. The refractory carbides and silicides do not equilibrate with the surrounding magma as it crystallizes under normally high oxygen fugacity, but remain as indicators of their formation. Such local pockets of low oxygen fugacity at moderate temperatures and pressures, leading to the geologic Si-C-O pathway, may explain the occurrence of small grains of highly reduced

refractory metal and carbide phases in many geologic settings without requiring their transport from extreme depth. In some cases, these refractory inclusions may have survived from earlier cycles of petrologic reactions.

Presolar dust particles have also been suggested to contain nanodiamond, graphite, titanium carbide, and other phases (Nguyen & Messenger, 2011) that may suggest condensation and evolution along a similar Si-O-C pathway. It is also tempting to speculate that in carbon-rich exoplanets containing some silicates, the Si-O-C pathway could be more prevalent.

5.3. UNANSWERED QUESTIONS AND FUTURE RESEARCH DIRECTIONS

Laboratory experiments and computational approaches need to address the following key questions. (1) Can silicate melts or glasses containing significant carbon concentrations resulting from the substitution of carbon for oxygen in mixed-bond tetrahedra be synthesized either directly or by the heating of PDC-like nanoceramics? Low oxygen fugacity (several orders of magnitude below the Fe/FeO buffer), moderately high temperature (1500–2000 °C), and pressure just high enough to suppress the gas formation that is a driving force for carbothermic reduction of silica (1–5 GPa) would be good starting points for such a study. (2) Can diamond (as micron-sized or larger crystals, nanodiamond, or with carbonado-like textures) be formed by the evolution of the Si-O-C nanoceramics? Can such diamond form and persist metastably outside the normal diamond stability field? (3) How do the Si-O-C nanoceramics transform, metamorphose, or weather under geologic conditions in contact with minerals and fluids? Do the silica-rich nanodomains disappear while the carbon-rich domains remain (as moissanite, graphite, or diamond)? Do the carbides and silicides formed by metal addition persist? Such experiments can be performed starting with synthetic and well-characterized PDC starting materials.

The occurrences described above have several features in common that make them candidates for a geologic Si-O-C pathway of carbon incorporation. These include high silica content and possible high carbon content in the parent rocks and low oxygen fugacity during impact or volcanism. The recovered natural materials should be examined in more detail by state-of-the-art analytical and structural techniques to seek evidence of carbon incorporation via mixed $\text{SiC}_x\text{O}_{4-x}$ bonding. Silicate phases (especially glass or its devitrification/alteration products), carbon phases (including both graphite and diamond), and silicon carbide grains and their inclusions should all be examined together, preferably when they originally are in close contact in a specimen rather than as isolated, recovered grains that may have come from different

environments. Given the age and likely alteration of the initial materials, this is a difficult task of mineralogical forensics and requires the collaboration of the geologic, planetary, and materials communities.

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