Deep Earth Carbon Reactions Through Time and Space

CATHERINE MCCAMMON[1], HÉLÈNE BUREAU[2],

H. JAMES CLEAVES[3,4,5], ELIZABETH COTTRELL[6], SUSANNAH M. DORFMAN[7], LOUISE H. KELLOGG[8], JIE LI[9], SAMI MIKHAIL[10], YVES MOUSSALLAM[11], CHRYSTELE SANLOUP[12], ANDREW THOMSON[13], ALBERTO VITALE BROVARONE[2,14]

1: Universität Bayreuth, Bayerisches Geoinstitut, Bayreuth, Germany

2: Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD UR206, 75005 Paris, France

3: Blue Marble Space Institute for Science, 1001 4th Ave, Suite 3201, Seattle, WA 98154, USA

4. Institute of Advanced Study, 1 Einstein Drive, Princeton, NJ 08540, U.S.A.

5: Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

6: Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington DC 20560, USA

7: Department of Earth and Environmental Sciences, Michigan State University, East Lansing, MI, USA

8: Department of Earth and Planetary Sciences, University of California, Davis, CA, USA

9: Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI, USA

10: School of Earth and Environmental Science, University of St Andrews, United Kingdom

11: Laboratoire Magmas et Volcans, Univ. Blaise Pascale – CNRS – IRD, OPGC, 63000 Clermont-Ferrand, France

12: Sorbonne Université, CNRS, UMR 7193, Institut des Sciences de la Terre de Paris, 4 place Jussieu, 75005 Paris, France

13: Department of Earth Sciences, University College London, United Kingdom

14: Dipartimento di Scienze della Terra, Università degli Studi di Torino, Italy

ABSTRACT

Reactions involving carbon in the deep Earth have limited manifestation on Earth's surface, yet they have played a critical role in the evolution of our planet. The metal-silicate partitioning reaction promoted carbon capture during Earth's accretion and may have sequestered substantial carbon in Earth's core. The melting/freezing reaction involving iron-carbon liquid could have contributed to the growth of Earth's inner core and provided power for the geodynamo that may continue to the present day. The redox melting/freezing reaction largely controls the movement of carbon in the modern mantle, and reactions between carbonates and silicates in the deep mantle also promote carbon mobility. The ten-year activity of the Deep Carbon Observatory has made important contributions to our knowledge of how these reactions are involved in the cycling of carbon throughout our planet, both past and present, and helped to identify gaps in our understanding that motivate and give direction to future studies.

Keywords: inner core, geodynamo, subduction, diamond, carbonate, carbon-rich fluids and melts, oxygen fugacity, metal-silicate partitioning, redox freezing and melting

INTRODUCTION

Although most people know there is carbon in the atmosphere, mainly due to the rising threat of climate change, few are aware that the amount of carbon in the atmosphere is small compared to that stored in other surface reservoirs (e.g., the oceans and upper crust) and that the amount of carbon in the atmosphere (and other surface reservoirs combined) is probably extremely small compared to that contained in Earth's deep subsurface. Chemical reactions involving carbon in surface reservoirs are "visible" in the sense that many of the reactants and products can be directly measured, and hence monitored, over space and time. The geological record shows that many surface reactions involving carbon have operated over geological time at least since the Archean, and have played a major role in maintaining the habitability of our planet (Hessler, 2011). The "Earth in Five Reactions" initiative selected the five most important reactions involving carbon (Li et al., 2018) and all can be characterized as "visible" reactions in that all manifest in some way on Earth's surface.

Current estimates based on mantle-derived samples and phase equilibria in carbon-containing systems suggest that at least 90% of Earth's carbon is sequestered in the mantle and core (e.g., Dasgupta and Hirschmann, 2010). The carbon in these remote regions of our planet also undergoes chemical reactions, but these reactions are essentially "invisible" since they have limited manifestation on Earth's surface. The nature of deep Earth carbon reservoirs and cycling has changed over geologic time scales and depths within Earth, and so has the prevalence of geochemical reactions involving carbon. How are deep Earth reactions important to the past and future evolution of our planet? This paper provides a snapshot of perspectives from those attending the "Earth in Five Reactions" workshop through a survey of deep Earth carbon reactions, focusing on what we know and don't know, and especially what we would like to know.

EARTH ACCRETION AND EARLY DIFFERENTIATION

How much carbon is in the core?

The key reaction that governed the capture of carbon when Earth accreted from the solar nebula around 4.5 billion years ago is metal-silicate partitioning:

$$CO_2 \text{ (silicate)} + 2\ Fe \text{ (alloy)} = C \text{ (alloy)} + 2\ FeO \text{ (silicate)}. \quad (1)$$

But where did the carbon come from? Carbon is a product of stellar nucleosynthesis that was subsequently released and dispersed through supernova explosions and eventually condensed into polyatomic compounds (Henning and Semenov, 2013). Even before accretion began, the formation of chondritic parent bodies fractionated carbon abundance away from solar nebula concentrations through processes including reaction 1.

The volatility of carbon varies hugely between its wide variety of oxidation states and compounds. Gaseous species such as methane (oxidation state -4) and carbon monoxide (oxidation state +2) are among the most volatile, while solid forms such as iron carbide and graphite/diamond (oxidation state 0) are among the least volatile. High-temperature processing would have removed volatile forms of carbon from planetary building blocks, while inorganic carbon phases (graphite/diamond, carbides, and carbonates) would have been preserved during low temperature planetesimal-forming collisions. Melting and subsequent solidification reactions (including reaction 1) would have produced differentiated chondritic bodies with metallic cores and rocky mantles (which are observed today as asteroids). Thus, while Earth's deep carbon cycle began with chondrites, it was only after the formation of planetesimals that it really got going.

Core formation likely started while Earth was still accreting (Fig. 1). Carbon strongly partitions into metallic melts relative to silicate melts (e.g., Dasgupta et al., 2013) and therefore is expected to have entered Earth's iron-rich core in abundance. Carbon steel and cohenite, $(Fe,Ni)_3C$, in iron meteorites are natural examples of iron-carbon alloys that demonstrate the affinity of carbon for metal-rich phases. At the conditions under which Earth's core formed, the partition coefficient of carbon between metal and silicate ($D_{metal/silicate}$) ranges from a few hundred to several thousand (e.g., Dasgupta et al., 2013), implying that around 90% of the carbon that was accreted to Earth prior to core segregation would go into the core.

The presence of carbon in the core can help to explain a number of geophysical observations. As a light element, carbon can partially account for the density deficit of the core with respect to pure iron or iron-nickel alloy. Adding carbon to iron can also help to match observed seismic velocities of the outer core due to increased compressional wave velocity relative to liquid iron (Nakajima et al., 2015). In addition, carbon depresses the melting point of iron and therefore its presence in the core may be partially responsible for the coexistence of a molten core and a mostly solid mantle at the core-mantle boundary (Morard et al., 2017).

The amount of carbon that can be present in the core may be limited by a number of processes. The extent of chemical exchange between the core and mantle may be restricted if Earth accreted from planetesimals with pre-differentiated cores that rapidly sank to the center of the planet, and some carbon may have been retained by the primordial atmosphere and not have participated in the reaction between metal and silicate (Bergin et al., 2015). Furthermore, a large fraction of Earth's carbon may have been delivered to Earth after core segregation was nearly complete, and may now reside in Earth's mantle (Dasgupta et al., 2013). These considerations could lead to a core that contained no carbon at all, although this is unlikely given the strong affinity of carbon for iron-alloy.

Further constraints on the carbon content of Earth's core may come from improved accretion models that combine astrochemical and geochemical studies (e.g. Bergin et al., 2015) and from new data on the physical properties and chemical behavior of carbon-bearing phases under deep Earth conditions (e.g., Shahar et al., 2016; Zhang et al., 2018). These are important points to resolve to determine whether the core is the dominant reservoir of terrestrial carbon.

FORMATION OF THE INNER CORE

Does carbon drive the Earth's geodynamo?

The inner core likely solidified at least one billion years after accretion of Earth was complete (Labrosse et al., 2001), and if carbon were involved, the key reaction would be

$$FeC_x \text{ (liquid)} = FeC_y \text{ (liquid)} + Fe_7C_3, \text{ where } y < x. \qquad (2)$$

This is a simplified expression that describes the partitioning of carbon at the outer core-inner core boundary during solidification of the inner core, although other alloying elements such as nickel, cobalt, sulfur, oxygen, and silicon may also have been involved (e.g., Wood et al., 2013). Reaction 2 implies that the molten core must be on the carbon-rich side of the iron-carbon eutectic (Fig. 2). In this case, the reaction describes the extraction of a crystalline iron-carbide from a liquid core, when it cooled to reach the liquidus temperature.

Earth's magnetic field is generated by the geodynamo, which is driven primarily by the growth of the solid inner core (see Buffett, 2000 and references therein). Compositional convection (rather than thermal convection) likely provides the major source of energy for the geodynamo through melting/freezing at the inner core boundary. Cooling causes crystallization at the inner core boundary while the residual liquid moves upwards (Fig. 2). We note that growing a carbide inner core might not generate sufficient chemical buoyancy to power the geodynamo, however. In a simplified iron-carbon binary system, solidification of iron carbide leaves behind a more iron-rich liquid, which might not be buoyant relative to outer core liquid (Fig. 2). However other light elements such as sulfur may partition favorably into the residual liquid and drive buoyancy upward (Buffett, 2000).

The hypothesis of a carbide inner core was proposed by Wood (1993) on the basis of the thermodynamic prediction that Fe_3C is the liquidus phase at inner core pressures and that the density of Fe_3C matches that of the inner core. A carbide inner core would imply that the core would be by far the largest carbon reservoir in Earth, accounting for more than 90% of the total carbon in the planet (e.g., Chen et al., 2014). Subsequent studies showed that the eutectic composition of the iron-carbon binary shifts to lower carbon content with increasing pressure (Lord et al., 2009), although not all studies agree that the core contains sufficient carbon to stabilize iron carbide in the liquidus (Fei and Brosh, 2014). Several studies report that Fe_3C and/or Fe_7C_3 may be unique in explaining the anomalously low shear wave velocity of the inner core, thus providing further support for a carbide inner core (Chen et al., 2014; Prescher et al., 2015). Theoretical studies, however, suggest that Fe_7C_3 is too light and/or too fast compared with the core (e.g., Mookherjee et al., 2011), and that exceptionally low shear velocities of the inner core could instead reflect softening close to the melting point (Martorell et al., 2013). Further studies are required to test models proposing carbide as a dominant carbon-bearing phase of the inner core.

MODERN EARTH

Carbon phases in the current mantle span the range from reduced solid forms that are relatively immobile (diamond, graphite, carbide) to oxidized liquid phases that are highly mobile (carbonated melt, carbon dioxide). Carbon transitions between these different forms through redox reactions, where one of the most important is redox melting/freezing:

$$MgCO_3 + 2\ Fe = 3\ (Fe_{2/3}Mg_{1/3})O + C. \qquad (3)$$

The forward freezing reaction produces diamond by reduction of carbonate subducted from Earth's surface while the reverse melting reaction generates carbonate through oxidation of diamond (e.g., Foley, 2010; Rohrbach and Schmidt, 2011).

How does redox freezing/melting influence carbon degassing/ingassing?

Carbonate redox melting and freezing reactions largely control the movement of carbon in the present day mantle. The oceanic crust has likely been subducting for the majority of Earth's history and is the dominant mechanism of carbon ingassing to the mantle from surface reservoirs. Redox freezing occurs where the subducting slab is relatively oxidized and the surrounding mantle is reduced (e.g., Frost and McCammon, 2008) (Fig. 3). As carbon migrates from the slab to the mantle, it encounters a strong redox gradient and reacts to form native carbon (reaction 3). This native carbon – diamond, graphite, carbide or metal alloy – is immobile, but can be carried to shallower depths by mantle upwelling. Because the oxidation state of the mantle increases with decreasing pressure, native carbon in an ascending mantle eventually reacts to form carbonated melt via redox melting at depths of ~150 km (e.g., Stagno et al., 2013). After this reaction, carbon is again oxidized and mobilized in carbonatite and carbonated silicate melts or emplaced in the lithosphere as carbonate (Fig. 3). The transport of carbon from the mantle to the surface as diamond in kimberlites or carbonatitic/carbonated melts carries key information to the surface about the deep carbon cycle, deep redox cycles, and the composition of the Earth. While most studies support the occurrence of a redox freezing/melting cycle, the quantities of carbon involved remain an open question.

What reactions occur between carbonates and silicates?

The stability of carbonates, including their reactivity with silicates, depends strongly on composition in addition to pressure and temperature, which in turn controls transport of carbon through the mantle. The strong affinity of calcium for silicate perovskite relative to carbonate leads to reactions such as:

$$CaCO_3 + MgSiO_3 = MgCO_3 + CaSiO_3 \tag{4}$$

at lower mantle depths (Biellmann et al., 1993; Seto et al., 2008). For silica-rich lithologies, reduction of carbonate to diamond has been observed in high-pressure experiments:

$$MgCO_3 + SiO_2 = MgSiO_3 + C + O_2 \tag{5}$$

(Seto et al., 2008; Maeda et al., 2017), and magnesite, $MgCO_3$, has been observed to react with metallic iron to produce reduced phases (Dorfman et al., 2018), but the reactivity of iron-bearing carbonates with silica remains to be investigated. Oxygen fugacity plays a major role in determining the stability of reactions involving iron, but control of redox conditions within the diamond anvil cell is still in its infancy. The strong link between oxygen fugacity and properties such as the composition of fluids and melts, however, motivates development of new techniques for high-pressure experiments.

What is the composition of carbon-bearing fluids and melts?

Diamond-hosted fluids from the mantle represent the only direct samples of primary mantle fluids, and thus provide a unique insight regarding the nature of carbonaceous fluids from the mantle. Mantle diamond formation usually occurs within the sub-cratonic lithospheric mantle, but deeper samples are also known (e.g., Shirey et al., 2013). Diamondforming fluids can be trapped as micro-inclusions along the surfaces of diamond fibers and surrounding diamond-hosted mineral inclusions, especially abundant in fibrous diamonds (Navon et al., 1988), but also found in gem diamonds from the peridotite and eclogitic suites (e.g., Jablon and Navon, 2016).

Carbon-rich and silica-poor melts generated by low degree partial melting are considered to be one of the main hosts of carbon in the upper mantle. Depending on their composition, they can contain several tens of weight percent of carbon dioxide which can remain dissolved in the melt until very low pressure (e.g., Moussallam et al., 2015). These melts are considered to evolve during ascent, becoming progressively silica-rich as they react with the mantle (e.g., Dasgupta and Hirschmann, 2010), yet they might also stall and pond, potentially accumulating at the lithosphere-asthenosphere boundary and explaining the so-called low velocity zone (e.g., Sakamaki et al., 2013). The reason that carbonated melts might pond in one case and migrate upwards in another remains to be fully elucidated. Due to their elevated amounts of carbon dioxide (several tens of weight percent), carbonated melts have a peculiar molecular structure with a remarkably polymerized silicate sub-network cohabiting with a carbonate sub-network (Moussallam et al., 2016). This structure can explain the high electrical conductivity of carbonated melts (Sifré et al., 2014) and hints at peculiar physical properties as a function of their carbon content (Moussallam et al., 2016). Future challenges lay in better characterizing their physical properties to understand how low-degree partial melts connect and migrate along grain boundaries.

Experiments devoted to growing diamonds in the laboratory show that water may be an important player in mobile carbonated melts or fluids that percolate the lithosphere (e.g., Bureau et al., 2018). Diamonds are exceptional witnesses for the deep carbon cycle because they form in all silicate reservoirs (from deep crust to lower mantle), and water is found in diamonds from every depth (e.g., Pearson et al., 2014; Palot et al., 2016). Open questions include: Are these hydrous fluids/melts local (i.e., only in subduction zones) or do they percolate through the whole mantle? Is diamond formation in the mantle a redox reaction (carbonate reduction, equation 3) as suggested by recent experimental studies (Bureau et al., 2018)? Or is it a carbon precipitation process involving simple oxygen-conserving reactions (Stachel et al., 2017)? Or both?

To conclude, it still remains to be determined if diamonds reflect ubiquitous precipitation from methane- and carbon dioxide-bearing water-rich fluids (e.g., Smit et al., 2016), or if diamonds are formed exclusively by carbonate-bearing and methane-free oxidized fluids or melts, or something else altogether.

DISCUSSION

How much carbon is in the deep mantle?

Subduction feeds Earth's mantle with crustal carbon in the form of carbonate minerals and organic carbon. Current estimates of carbon entering subduction zones range between 40 to 66 Mt/year (Kelemen and Manning, 2015), but it is uncertain how much of this carbon actually reaches the deep mantle. Until 2015, most models considered decarbonation reactions and melting as the dominant processes mobilizing carbon from subducting slabs, and predicted that about half of subducted carbon is recycled into the deep mantle (e.g., Dasgupta and Hirschmann, 2010). These fluxes were then reevaluated by Kelemen and Manning (2015) by considering the solubility of subducted carbonates in aqueous fluids. The authors estimated that only a negligible amount of crustal carbon (lower bound 0.0001 Mt/y) is recycled into the deep mantle. Based on the higher estimated carbon flux degassing from subducting slabs compared to the flux from arc volcanoes and diffuse outgassing into the atmosphere, the authors argued in favor of carbon storage within the lithospheric mantle above subducting slabs. Such estimates, however, remain highly uncertain, and upper bounds of subducted carbon reaching the deep mantle are roughly 80% of total subducted carbon (Kelemen and Manning, 2015).

Experimental investigations that simulate downwelling of slab material generally agree that carbonated eclogitic assemblages will successfully transport the majority of their carbonate to depths of at least ~ 300 km, but melting will occur before 600 km is reached as slab geotherms intersect the solidus of carbonated mafic assemblages (e.g., Thomson et al., 2016) (Fig. 3). Inclusions of carbonate minerals in diamonds, on the other hand, provide evidence that at least some carbon survives (e.g., Brenker et al., 2007). Inclusions in diamonds from greater depths provide evidence for carbon in the lower mantle (e.g., Harte et al., 1999; Nestola et al., 2018), but the question remains as to whether such inclusion-bearing diamonds are rarities, or the tip of the proverbial iceberg. Nevertheless, recent phase diagrams suggest that cold subducting slabs could stabilize carbonates to mid-lower mantle depths, especially considering iron enrichment due the spin transition (Cerantola et al., 2017), and others have argued that oxidizing conditions and slow kinetics within subducting slabs may also facilitate carbonate transport to great depths (Martirosyan et al., 2016).

The ten-year activity of the Deep Carbon Observatory has led to significant improvements in the definition of open-system, fluid-mediated processes modulating the flux of subducted carbon into the deep mantle and the speciation of deep carbon-bearing fluids. These include, among others, processes directly related to the five reactions selected by the “Earth in Five Reactions” initiative (Li et al., 2019). Most available flux estimates are based on closed-system behavior and still cannot account for reactive fluid flow processes expected from theoretical models and confirmed by the study of natural samples. Assessing the significance of these processes on the residence time of subducted crustal carbon and its recycling into the deep mantle represents a current challenge for the deep carbon community.

IMPLICATIONS

The reactions presented in this paper complement the five reactions selected by the "Earth in Five Reactions" initiative (Li et al., 2018). All of the reactions mentioned here are "invisible" in the sense that they have limited manifestation on Earth's surface. Earth would be a different planet, however, if none of these reactions had taken place within its history. Without reaction 1 the amount of carbon retained during accretion would be considerably lower. Without reaction 2 the driving force for the geodynamo would likely be weaker and perhaps there would be no geomagnetic field. Without reactions 3-5 the cycling of volatile elements, especially oxygen, would take place along different pathways and cause significant changes to volatile reservoirs such as Earth's atmosphere, possibly altering the conditions for life. In other words, without the deep carbon reactions presented in this paper, there would likely be no one around to debate the five most important carbon reactions.

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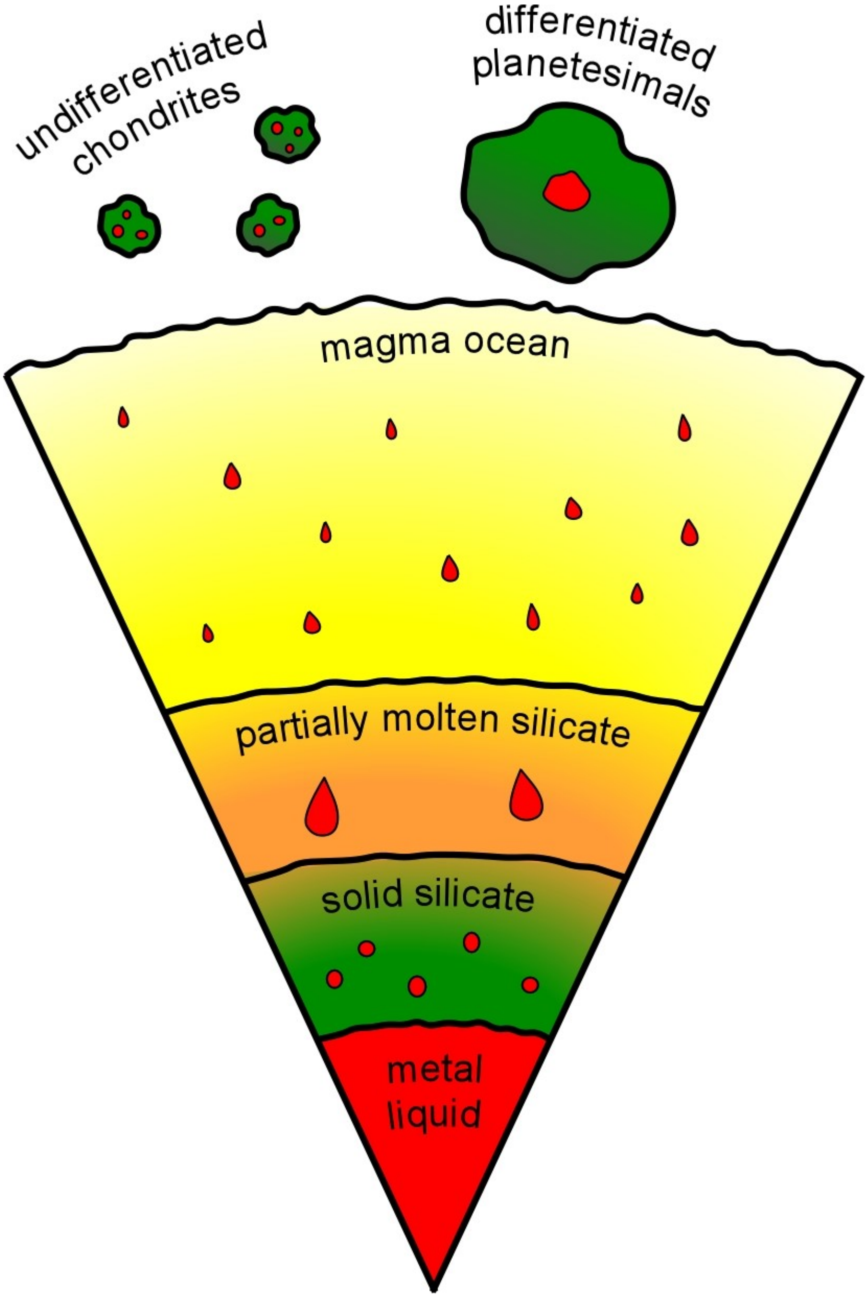

FIGURE 1. Carbon assimilation during Earth's accretion and core formation. Metal-silicate partitioning (reaction 1) takes place at the interface between silicate and metallic liquid in the accreting Earth and during differentiation of planetesimals (after Dasgupta, 2013). Carbon-containing material (mainly carbide and metallic melt) is indicated in red.

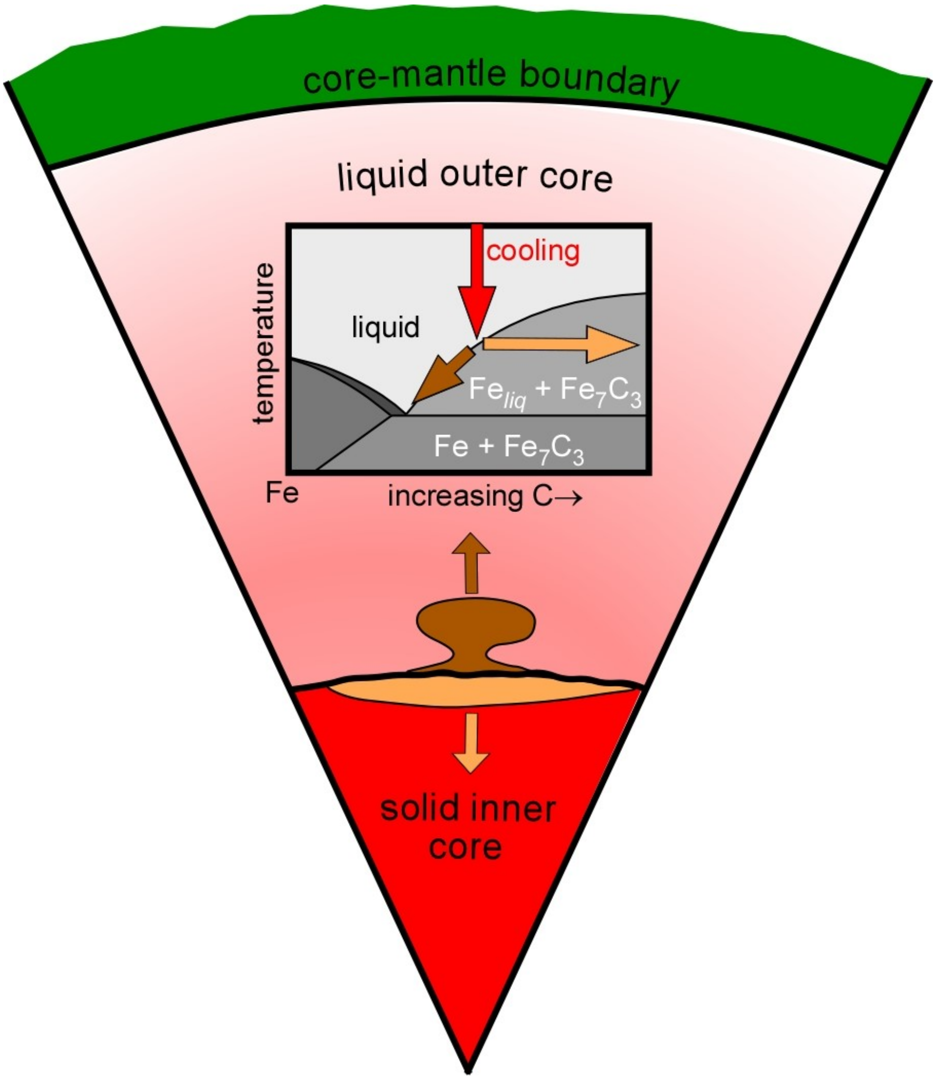

FIGURE 2. Carbon involvement during growth of the inner core. Iron-carbon melting and solidification (reaction 2) takes place at the boundary between the inner and outer core. On cooling (see inset phase diagram), the assemblage separates into residual liquid (dark brown) and crystalline Fe_7C_3 (light brown). The residual liquid will rise if it is buoyant relative to outer core liquid.

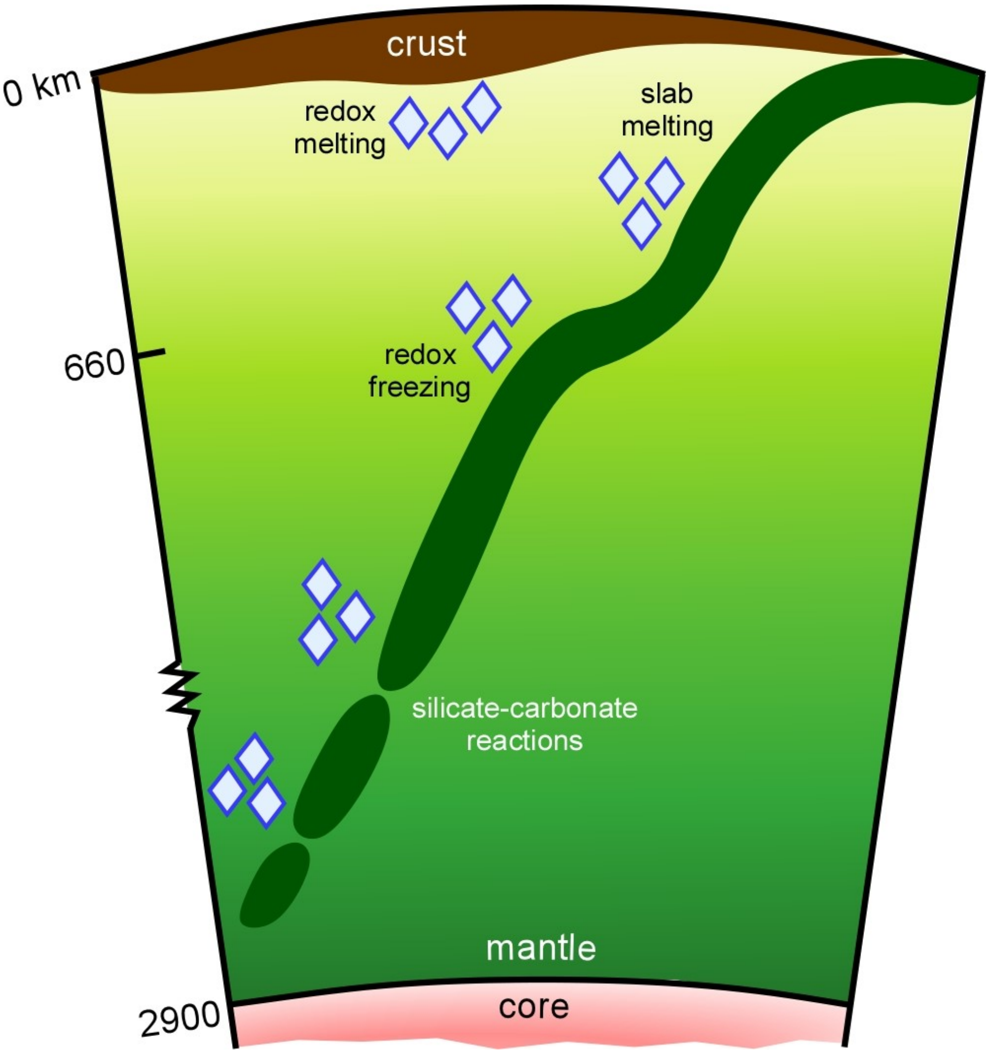

FIGURE 3. Selected redox reactions on modern Earth. Carbonate in subducting slabs is reduced to diamond via redox freezing, while native carbon (diamond, carbide) in ascending melts reacts to form carbonated melt via redox melting (reaction 3). Diamond formation can also occur through slab melting (Thomson et al., 2016), as well as from silicate-carbonate reactions taking place in the lower mantle (reactions 4 and 5). The thickness of the crust and subducting slab is vertically exaggerated for clarity.