Revision 1
Earth in Five Reactions *Special Collection DEEP EARTH REACTIONS*
MCCAMMON et al.

Deep Earth Carbon Reactions Through Time and Space

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

H. JAMES CLEAVES II[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, 95440 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, USA

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, 48824, USA

8: Department of Earth and Planetary Sciences, University of California, Davis, CA, 95616, USA

9: Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI, 48109, USA

10: School of Earth and Environmental Science, University of St Andrews, St Andrews, Fife, KY16 9AL, 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, London WC1E 6BT, United Kingdom

14: Dipartimento di Scienze della Terra, Università degli Studi di Torino, 10125 Torino, Italy

[†] deceased

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 freezing reaction involving iron-carbon liquid could have contributed to the growth of Earth's inner core and the geodynamo. 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, not all are aware that the amount of carbon in the atmosphere is around one hundred thousand times less than that stored in other surface reservoirs (e.g., the oceans and continents) (Falkowski et al., 2000), and that the amount of carbon in Earth's interior (mantle and core) is thought to be at least three million times greater than the amount in the atmosphere (Dasgupta and Hirschmann, 2010). 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., 2019) 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 the mantle contains at least as much carbon as the crust while the core may contain up to 90% of Earth's carbon (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 direct influence 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 and distribution of carbon when Earth accreted from the solar nebula around 4.5 billion years ago is metal-silicate partitioning (e.g., Dasgupta, 2013):

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

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, processes such as ice formation and devolatilization changed volatile element abundances relative to solar nebula abundances (e.g., Marty et al., 2013).

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 the building blocks, it really got going after the formation of planetismals.

Core formation likely started while Earth was still accreting and may have continued post-accretion (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 is believed to have formed, the partition coefficient of carbon between metal and silicate ($D_{\text{metal/silicate}}$) ranges from a few hundred to several thousand (e.g., Dasgupta et al., 2013), implying that around 90% of the carbon accreted to Earth prior to core segregation should have entered the core. Current estimates suggest a maximum concentration of ~1 wt% carbon in Earth’s core (Wood et al., 2013).

The presence of carbon in the core can help 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 have been limited by a number of processes. The extent of chemical exchange between the core and mantle would have been 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 processes could have led 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

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

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 the density match between Fe_3C and 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 uniquely explain 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 its sound velocity is 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:

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

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?

Redox melting of carbon or carbide and freezing of carbonate largely control the movement of carbon in the present day mantle. Regardless of when plate tectonics started (see, for example, Korenaga, 2013), subduction of oceanic crust 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 oxygen fugacity of the mantle decreases with increasing depth in the deep upper mantle and below (e.g., Frost and McCammon, 2008), 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:

$$CaCO_3 \text{ (calcite)} + MgSiO_3 \text{ (silicate)} = MgCO_3 \text{ (magnesite)} + CaSiO_3 \text{ (silicate)} \qquad (4)$$

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:

$$MgCO_3 \text{ (magnesite)} + SiO_2 \text{ (stishovite)} = MgSiO_3 \text{ (silicate)} + C \text{ (diamond)} + O_2 \qquad (5)$$

(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). The reactivity of iron-bearing carbonates with silica is only just starting to be investigated, however (Drewitt et al., 2019). 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). Diamond-forming 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). 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 lie 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) might be 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).

After ten years of activity, efforts stemming from the Deep Carbon Observatory have led to significant improvements in identifying (a) the speciation of deep carbon-bearing fluids, and (b) the open-system, fluid-mediated processes that control the subducted carbon flux into the deep mantle. The identified reactions include 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., 2019). 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 and form of carbon retained during accretion would be considerably different. Without reaction 2 the driving force for the geodynamo would not be the same 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.

ACKNOWLEDGEMENTS

We dedicate this paper to the memory of our co-author, colleague and close friend, Louise Kellogg. The authors acknowledge partial support from the Sloan Foundation grant G-2016-7157. We thank anonymous reviewers for their constructive comments that improved the paper.

REFERENCES CITED

Bergin, E.A., Blake, G.A., Ciesla, F., Hirschmann, M.M., and Li, J. (2015) Tracing the ingredients for a habitable earth from interstellar space through planet formation. Proceedings of the National Academy of Sciences USA, 112, 8965-8970.

Biellmann, C., Gillet, P., Guyot, F., Peyronneau, J., and Reynard, B. (1993) Experimental evidence for carbonate stability in the Earth's lower mantle. Earth and Planetary Science Letters, 118, 31-41.

Brenker, F.E., Vollmer, C., Vincze, L., Vekemans, B., Szymanski, A., Janssens, K., Szaloki, I., Nasdala, L., Joswig, W., and Kaminsky, F. (2007) Carbonates from the lower part of transition zone or even the lower mantle. Earth and Planetary Science Letters, 260, 1-9.

Buffett, B.A. (2000) Earth's core and the geodynamo. Science, 288, 2007-2012.

Bureau, H., Remusat, L., Esteve, I., Pinti, D.L., and Cartigny, P. (2018) The growth of lithospheric diamonds. Science Advances, 4: eaat1602, 1-5.

Cerantola, V., Bykova, E., Kupenko, I., Merlini, M., Ismailova, L., McCammon, C., Bykov, M., Chumakov, A., Petitgirard, S., Kantor, I., Svitlyk, V., Jacobs, J., Prescher, C., Rüffer, R., and Dubrovinsky, L. (2017) Stability of iron-bearing carbonates in the deep Earth's interior. Nature Communications, 8(15960), DOI: 10.1038/ncomms15960.

Chen, B., Li, Z., Zhang, D., Liu, J., Hu, M.Y., Zhao, J., Bi, W., Alp, E.E., Xiao, Y., Chow, P., and Li, J. (2015) Hidden carbon in Earth's inner core revealed by shear softening in dense Fe_7C_3. Proceedings of the National Academy of Sciences USA, 111, 17755–17758.

Dasgupta, R. (2013) Ingassing, storage, and outgassing of terrestrial carbon through geologic time. Reviews in Mineralogy and Geochemistry, 75, 183-229.

Dasgupta, R., and Hirschmann, M.M. (2010) The deep carbon cycle and melting in Earth's interior. Earth and Planetary Science Letters, 298, 1-13.

Dasgupta, R., Chi, H., Shimizu, N., Buono, A.S., and Walker, D. (2013) Carbon solution and partitioning between metallic and silicate melts in a shallow magma ocean: Implications for the origin and distribution of terrestrial carbon. Geochimica Cosmochimica Acta, 102, 191-212.

Dorfman, S.M., Badro, J., Nabiei, F., Prakapenka, V.B., Cantoni, M., and Gillet, P. (2018) Carbonate stability in the reduced lower mantle. Earth and Planetary Science Letters, 489, 84-91.

Drewitt, J., Walter, M., Zhang, H., McMahon, S., Edwards, D., Heinen, B., Lord, O., Anzellini, S., and Kleppe, A. (2019) The fate of carbonate in oceanic crust subducted into Earth's lower mantle. Earth and Planetary Science Letters, 511, 213-222.

Falkowski, P., Scholes, R.J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., K. Hibbard, Högberg, P., Linder, S., Mackenzie, F.T., III, B.M., Pedersen, T., Rosenthal, Y., Seitzinger, S., Smetacek, V., and Steffen, W. (2000) The global carbon cycle: A test of our knowledge of Earth as a system. Science, 290, 291-296.

Fei, Y., and Brosh, E. (2014) Experimental study and thermodynamic calculations of phase relations in the Fe–C system at high pressure. Earth and Planetary Science Letters, 408, 155-162.

Foley, S. (2010) A Reappraisal of Redox Melting in the Earth’s Mantle as a Function of Tectonic Setting and Time. Journal of Petrology, 52, 1363-1391.

Frost, D.J., and McCammon, C.A. (2008) The redox state of Earth's mantle. Annual Review of Earth and Planetary Sciences, 36, 389-420.

Harte, B., Harris, J.W., Hutchison, M.T., Watt, G.R., and Wilding, M.C. (1999) Lower mantle mineral associations in diamonds from São Luiz, Brazil. In Y. Fei, C.M. Bertka, and B.O. Mysen, Eds. Mantle Petrology: Field Observations and High-Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd, 6, p. 125-153. Geochemical Society, USA.

Henning, T., and Semenov, D. (2013) Chemistry in Protoplanetary Disks. Chemical Reviews, 113, 9016-9042.

Hessler, A.M. (2011) Earth's earliest climate. Nature Education Knowledge, 3(10), 24.

Jablon, B.M., and Navon, O. (2016) Most diamonds were created equal. Earth and Planetary Science Letters, 443, 41-47.

Korenaga, J. (2013) Initiation and evolution of plate tectonics on Earth: Theories and observations. Annual Review of Earth and Planetary Sciences, 41, 117-151.

Labrosse, S., Poirier, J.-P., and Mouël, J.-L.L. (2001) The age of the inner core. Earth and Planetary Science Letters, 190, 111-123.

Li, J., Redfern, S.A.T., and Giovannelli, D. (2019) Deep carbon cycle through five reactions. American Mineralogist, 104, 465-467.

Lord, O., Walter, M., Dasgupta, R., Walker, D., and Clark, S. (2009) Melting in the Fe-C system to 70 GPa. Earth and Planetary Science Letters, 284, 157-167.

Maeda, F., Ohtani, E., Kamada, S., Sakamaki, T., Hirao, N., and Ohishi, Y. (2017) Diamond formation in the deep lower mantle: a high-pressure reaction of $MgCO_3$ and SiO_2. Scientific Reports, 7:40602, DOI: 10.1038/srep40602.

Martorell, B., Vočadlo, L., Brodholt, J., and Wood, I.G. (2013) Strong premelting effect in the elastic properties of hcp-Fe under inner-core conditions. Science, 342, 466-468.

Martirosyan, N.S., Yoshino, T., Shatskiy, A., Chanyshev, A.D., and Litasov, K.D. (2016) The $CaCO_3$–Fe interaction: Kinetic approach for carbonate subduction to the deep Earth's mantle. Physics of the Earth and Planetary Interiors, 259, 1-9.

Marty, B., Alexander, C.M.O., and Raymond, S.N. (2013) Primordial origins of earth's carbon. Reviews in Mineralogy and Geochemistry, 75, 149-181.

Mookherjee, M., Nakajima, Y., Steinle-Neumann, G., Glazyrin, K., Wu, X., Dubrovinsky, L., McCammon, C.A., and Chumakov, A. (2011) High pressure behavior of iron carbide (Fe_7C_3)

at inner core conditions. Journal of Geophysical Research, 116, doi:10.1029/2010JB007819, 2011.

Morard, G., Andrault, D., Antonangeli, D., Nakajima, Y., Auzende, A.L., Boulard, E., Cervera, S., Clark, A., Lord, O.T., Siebert, J., Svitlyk, V., Garbarino, G., and Mezouar, M. (2017) Fe–FeO and Fe–Fe_3C melting relations at Earth's core–mantle boundary conditions: Implications for a volatile-rich or oxygen-rich core. Earth and Planetary Science Letters, 473, 94-103.

Moussallam, Y., Morizet, Y., Massuyeau, M., Laumonier, M., and Gaillard, F. (2015) CO_2 solubility in kimberlite melts. Chemical Geology, 418, 198-205.

Moussallam, Y., Florian, P., Corradini, D., Morizet, Y., Sator, N., Vuilleumier, R., Guillot, B., Iacono-Marziano, G., Schmidt, B.C., and Gaillard, F. (2016) The molecular structure of melts along the carbonatite–kimberlite–basalt compositional joint: CO_2 and polymerisation. Earth and Planetary Science Letters, 434, 129-140.

Nakajima, Y., Imada, S., Hirose, K., Komabayashi, T., Ozawa, H., Tateno, S., Tsutsui, S., Kuwayama, Y., and Baron, A.Q.R. (2015) Carbon-depleted outer core revealed by sound velocity measurements of liquid iron–carbon alloy. Nature Communications, 6: 8942, DOI: 10.1038/ncomms9942.

Navon, O., Hutcheon, I.D., Rossman, G.R., and Wasserburg, G.J. (1988) Mantle-derived fluids in diamond micro-inclusions. Nature, 335, 784-789.

Nestola, F., Korolev, N., Kopylova, M., Rotiroti, N., Pearson, D.G., Pamato, M.G., Alvaro, M., Peruzzo, L., Gurney, J.J., Moore, A.E., and Davidson, J. (2018) $CaSiO_3$ perovskite in diamond indicates the recycling of oceanic crust into the lower mantle. Nature, 555, 237-241.

Palot, M., Jacobsen, S.D., Townsend, J.P., Nestola, F., Marquardt, K., Miyajima, N., Harris, J.W., Stachel, T., McCammon, C.A., and Pearson, D.G. (2016) Evidence for water in the lower mantle from ferropericlase included in diamond. Lithos, 265, 237-243.

Pearson, D.G., Brenker, F.E., Nestola, F., McNeill, J., Nasdala, L., Hutchison, M.T., Matveev, S., Mather, K., Silversmit, G., Schmitz, S., Vekemans, B., and Vincze, L. (2014) Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature, 507, 221-224.

Prescher, C., Dubrovinsky, L., Bykova, E., Kupenko, I., Glazyrin, K., Kantor, A., McCammon, C., Mookherjee, M., Nakajima, Y., Miyajima, N., Sinmyo, R., Cerantola, V., Dubrovinskaia, N., Prakapenka, V., Rüffer, R., Chumakov, A., and Hanfland, M. (2015) High Poisson's ratio of Earth's inner core explained by carbon alloying. Nature Geoscience, 8, 220-223.

Rohrbach, A., and Schmidt, M.W. (2011) Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron redox coupling. Nature, 472, 209-212.

Sakamaki, T., Suzuki, A., Ohtani, E., Terasaki, H., Urakawa, S., Katayama, Y., Funakoshi, K.-i., Wang, Y., Hernlund, J.W., and Ballmer, M.D. (2013) Ponded melt at the boundary between the lithosphere and asthenosphere. Nature Geoscience, 6, 1041-1044.

Seto, Y., Hamane, D., Nagai, T., and Fujino, K. (2008) Fate of carbonates within oceanic plates subducted to the lower mantle, and a possible mechanism of diamond formation. Physics and Chemistry of Minerals, 35, 223-229.

Shahar, A., Schauble, E.A., Caracas, R., Gleason, A.E., Reagan, M.M., Xiao, Y., Shu, J., and Mao, W. (2016) Pressure-dependent isotopic composition of iron alloys. Science, 352, 580-582.

Shirey, S.B., Cartigny, P., Frost, D.J., Keshav, S., Nestola, F., Nimis, P., Pearson, D.G., Sobolev, N.V., and Walter, M. (2013) Diamonds and the geology of mantle carbon. Reviews in Mineralogy and Geochemistry, 75, 355-421.

Sifré, D., Gardés, E., Massuyeau, M., Hashim, L., Hier-Majumder, S., and Gaillard, F. (2014) Electrical conductivity during incipient melting in the oceanic low-velocity zone. Nature, 509, 81-85.

Smit, K.V., Shirey, S.B., Stern, R.A., Steele, A., and Wang, W. (2016) Diamond growth from C–H–N–O recycled fluids in the lithosphere: Evidence from CH4 micro-inclusions and δ13C–δ15N–N content in Marange mixed-habit diamonds. Lithos, 265, 68-81.

Stachel, T., Chacko, T., and Luth, R.W. (2017) Carbon isotope fractionation during diamond growth in depleted peridotite: Counterintuitive insights from modelling water-maximum CHO fluids as multi-component systems. Earth and Planetary Science Letters, 473, 44-51.

Stagno, V., Ojwang, D.O., McCammon, C.A., and Frost, D.J. (2013) The oxidation state of the mantle and the extraction of carbon from Earth's interior. Nature, 493, 84-88.

Thomson, A.R., Walter, M.J., Kohn, S.C., and Brooker, R.A. (2016) Slab melting as a barrier to deep carbon subduction. Nature, 529, 76-79.

Wood, B.J., Li, J., and Shahar, A. (2013) Carbon in the core: Its influence on the properties of core and mantle. Reviews in Mineralogy and Geochemistry, 75, 231-250.

Zhang, C., Lin, J.-F., Liu, Y., Feng, S., Jin, C., Hou, M., and Yoshino, T. (2018) Electrical resistivity of Fe-C alloy at high pressure: Effects of carbon as a light element on the thermal conductivity of the Earth's core. Journal of Geophysical Research: Solid Earth, 123, 3564-3577.

FIGURE CAPTIONS

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.

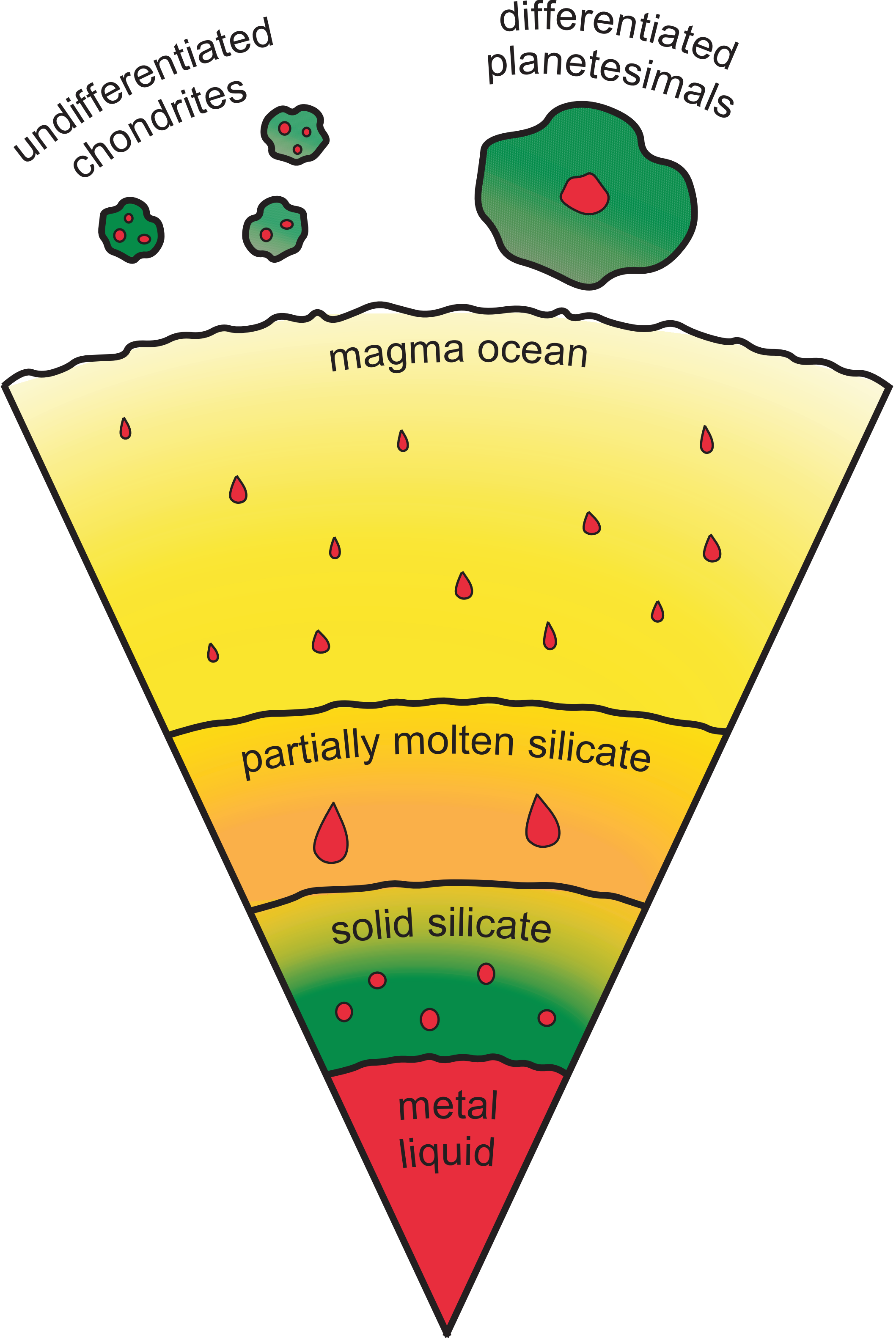
undifferentiated chondrites
differentiated planetesimals
magma ocean
partially molten silicate
solid silicate
metal liquid

Figure 1

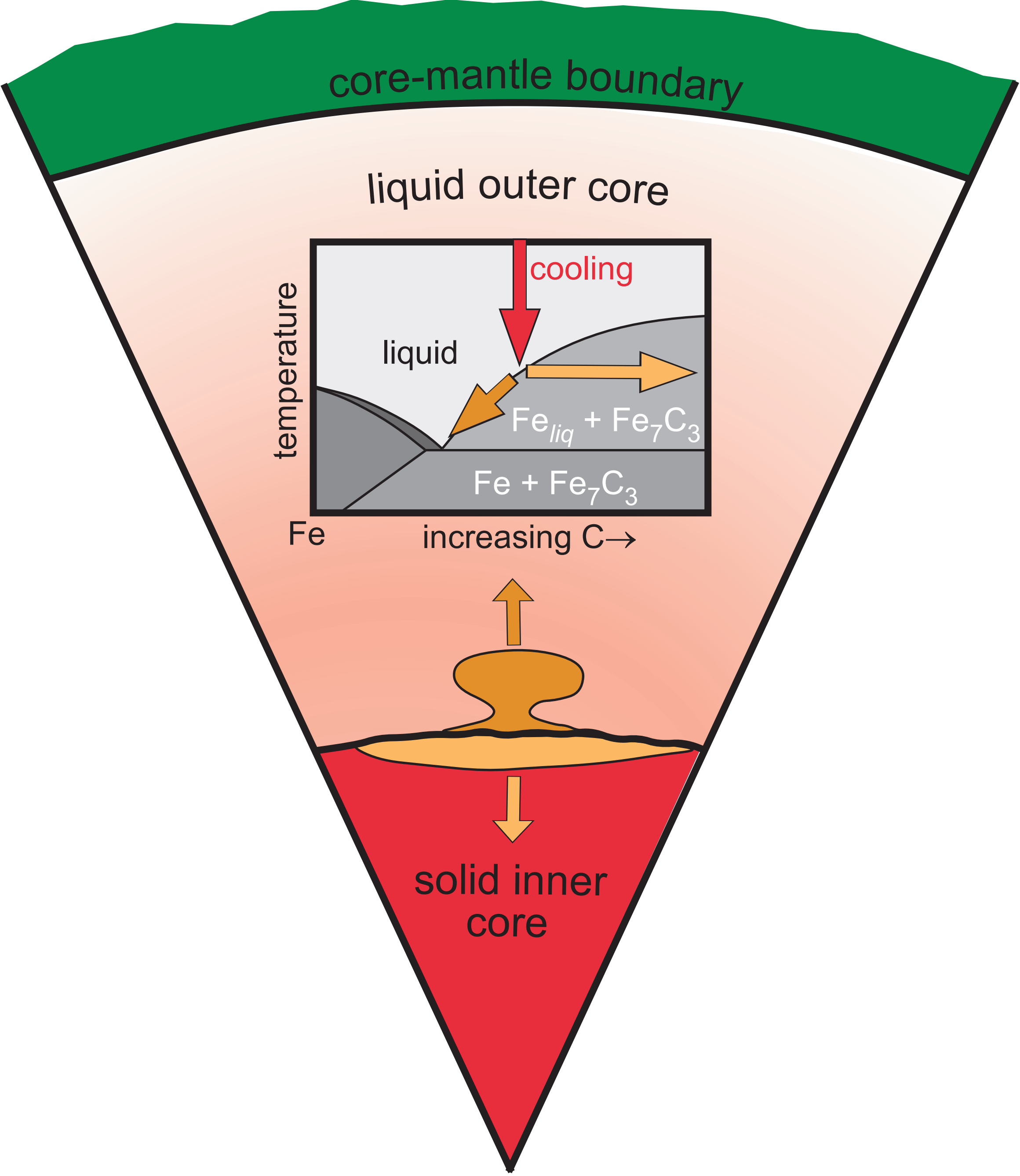
core-mantle boundary
liquid outer core
cooling
liquid
temperature
$Fe_{liq} + Fe_7C_3$
$Fe + Fe_7C_3$
Fe
increasing C→
solid inner
core

Figure 2

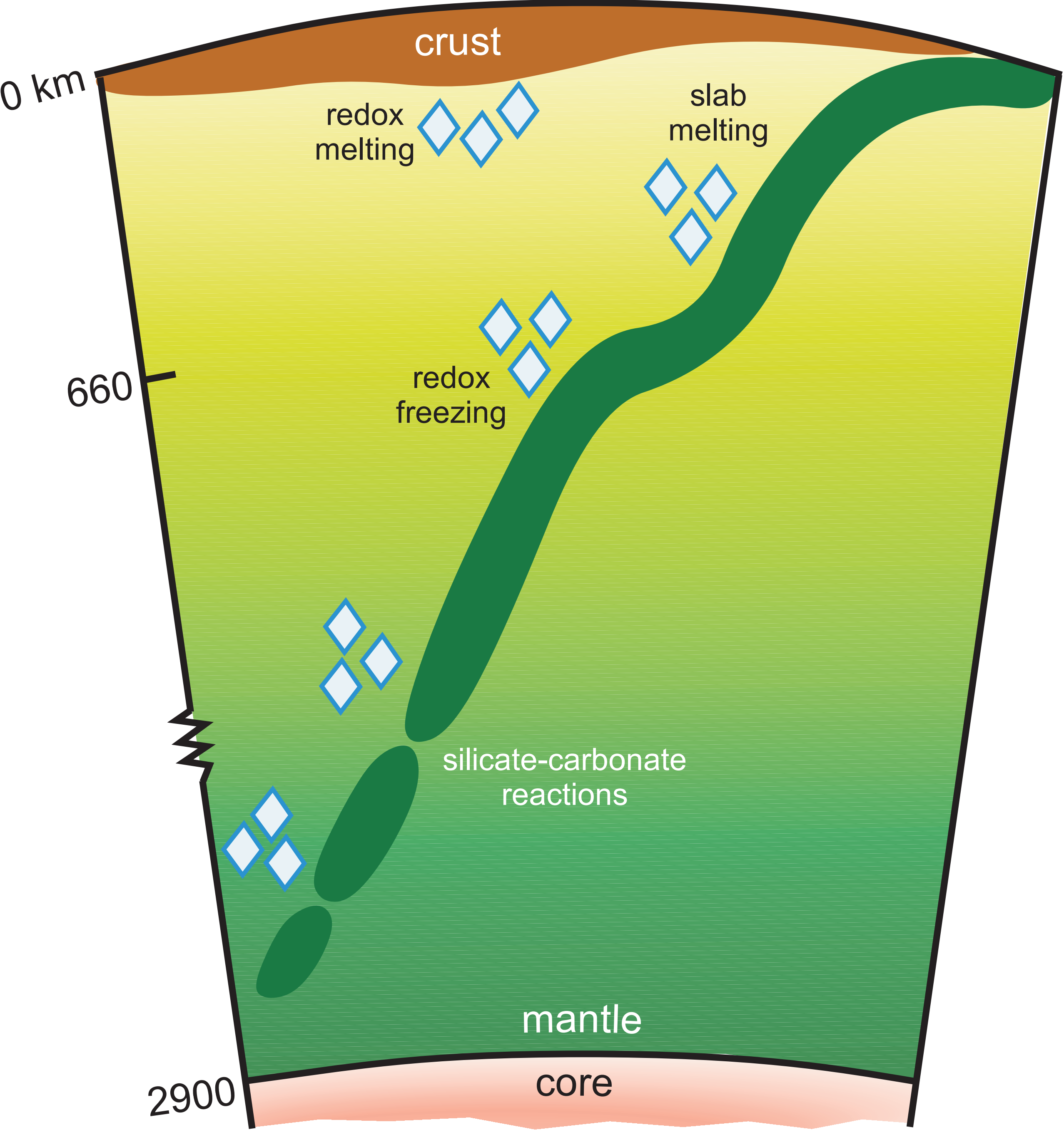
crust
0 km
redox
melting
slab
melting
660
redox
freezing
silicate-carbonate
reactions
mantle
2900
core

Figure 3