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Carbon in Earth's Interior

Craig E. Manning
Jung-Fu Lin
Wendy L. Mao
Editors

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PREFACE

Carbon in Earth's fluid envelopes—the atmosphere and hydrosphere—plays a fundamental role in our planet's climate system. It is also essential for the origin and evolution of life, for a large fraction of the energy we use, and for the multitude of carbon-based materials so essential to the modern world. Yet the source and original quantity of carbon in our planet is uncertain (Marty et al., 2013), as are the identities and relative importance of early chemical processes associated with planetary differentiation (e.g., the moon-forming impact, core formation, the onset of plate tectonics). Numerous lines of evidence point to the early and continuing exchange of substantial carbon between Earth's surface and its interior (Dasgupta, 2013), such as information carried by subducted carbon trapped in diamonds, mantle-derived magmas rich in carbon, carbonate-bearing rocks found in fossil subduction zones, and springs carrying deeply sourced carbon-bearing gases (Burton et al., 2013; Jones et al., 2013; Ni & Keppler, 2013; Shirey et al., 2013). Although quantifying the input and output fluxes is challenging, there is little doubt that a substantial amount of carbon resides in our planet's interior (Dasgupta and Hirschmann, 2010, Kelemen & Manning, 2015).

These uncertainties arise in part from continuing difficulties in establishing the forms, transformations, and movements of carbon in Earth's interior. The present volume provides a snapshot of recent work aimed at improving this picture. It presents research aimed at understanding the physical and chemical behavior of carbon-bearing materials at conditions relevant to Earth's interior – behavior that ultimately dictates the availability of this element so important to processes near our planet's surface.

The papers in this volume are a mix of reviews and reports of current research on the structure, stability, reactivity, and dynamics of carbon-based materials relevant to natural systems, as well as to allied substances that carry carbon, and the complex interactions between moving fluids, magmas, and rocks in Earth's interior. Carbon materials of Earth and planetary interest are found in a wide range of structural states (Hazen et al., 2013; Oganov et al., 2013). Of the many transformations between these states, one of the most profound is that induced by change from sp^2 to sp^3 bonding of carbon in a structure. This transformation occurs in native carbon (graphite to diamond), in CO_2 ices, carbonate minerals, and hydrocarbons. In Chapter 1, Lobanov and Goncharov review this transformation in a subset of these materials. A key point is that the sp^2-sp^3 change leads to higher coordination number and is promoted by high pressure, and is therefore encountered at the extreme pressures of planetary interiors. However, as shown by Tschauner (Chapter 2), diamond remains the only naturally sampled material that preserves carbon in sp^3-bonded sites. Tschauner reviews carbonaceous inclusions found in terrestrial diamonds delivered to the surface from the mantle, in some cases at high residual pressures. The crystalline forms run the gamut of carbon oxidation states: native carbon and carbides; oxidized carbon in CO_2 ices and carbonate minerals; and, not discussed by Tschauner, rare hydrocarbon inclusions as well (e.g., Sobolev et al., 2019), though the origins of such materials have in the past been ascribed to later, shallower processes.

Carbon's cosmochemical abundance and chemical behavior favor carbon as a potential light element in the core. If present, carbon would likely be strongly partitioned into the inner core, as Fe-carbide. While early work favored Fe_3C (cementite) as the likely inner-core carbide, recent studies advanced the idea that this phase is not stable at inner core conditions, and Fe_7C_3 is instead the more likely inner-core carbide. Takahashi et al. (Chapter 3) performed new experiments that show that Fe_3C is stable to inner core conditions. Both carbide phases may be present in the inner core and could be consistent with seismological observations.

Chen and Wang (Chapter 4) review the structure and physical properties of carbon-bearing Fe-Ni liquids at conditions relevant to planetary cores. Where present, carbon may play an important role in controlling structural transformation in Fe-Ni-C liquids.

Comparatively little carbon can be incorporated into silicates, and the mechanism(s) for accommodating even small amounts is poorly known. Navrotsky et al. (Chapter 5) discuss silicate-rich ceramics that incorporate carbon via substitution of C for O in the silica tetrahedron, the fundamental building block of the rock-forming silicate minerals and the structural backbone of silicate melts. Geologic pathways for production of such materials may include large impact events, and these materials may be precursors for some puzzling natural occurrences of silicon carbide and carbonado.

Oxidized carbon, as CO_2, is important to a wide range of geologic processes from the surface to the interior of Earth, and potentially other solar system objects and exoplanets. It is therefore essential to understand the behavior of CO_2 itself at elevated pressure and temperature. The properties and transformations of CO_2 gas, liquid, and supercritical fluid are relatively well understood compared to CO_2 ices. As with H_2O, compression of CO_2 at very low to very high temperature produces a wide range of ice structures, which display a remarkable variety of bonding environments that suggest surprising possibilities for the forms and transformations of CO_2 in planetary interiors. Chapters 6 and 7, by Santoro et al. and Yoo, present overviews of the current state of knowledge of high-pressure CO_2 phases and their structures and properties. Despite years of aggressive investigation, the equilibrium phase diagram remains elusive. Metastable states and surprising forms such as high-pressure amorphous phases persist, likely owing to a complex energy landscape with multiple local minima and challenging kinetics (e.g., Machon et al., 2014), as has recently been illustrated by Tulk et al. (2019) for H_2O ices. Nevertheless, it is clear that CO_2 phase space contains a rich variety of molecular ices that give way at high pressure to a polymerized, extended covalent structure, CO_2-V, in which *sp*^{3} carbon is tetrahedrally coordinated by oxygen in a silica-like structure. This structure raises the possibility of solid solution with SiO_2, but this has yet to be conclusively verified. The contrasting interpretations of some of the features and phases of the CO_2 system in the two chapters attests to the challenges of working on this important but kinetically sluggish and energetically complex chemical system.

Li et al. (Chapter 8) explore the role of carbon surfaces on H_2O ice and methane clathrate crystallization. Using classical molecular dynamics, they find that ice nucleation and growth depends strongly on the chemistry, crystallinity, and topography of the nucleating surface. Gas hydrates initially nucleate as amorphous clusters, but crystallinity increases with the size of the hydrate. The picture is highly complex on the molecular scale, and there appear to be numerous pathways for hydrate growth.

The primary solid storage site for oxidized carbon is in carbonate minerals. The carbonate minerals exhibit a wide range in structures and bonding environments for carbon, as seen in CO_2. Merlini et al. (Chapter 9) review research over the last 10–15 years that reveals the complex pressure and temperature dependence of the crystal chemistry of carbonate minerals. From Earth's surface to the mid mantle, an essential building block of carbonate minerals is the trigonal CO_3^{-2} ion. In addition to pressure-induced transformations such as calcite to aragonite, and aragonite to post-aragonite, arrays of carbonate ions exhibit many subtle changes in geometry that give rise to a host of subtly different stable and metastable mineral polymorphs. At pressures of the mid-mantle and greater, trigonal coordination of C by O gives way to tetrahedral coordination, with attendant transformation to crystal structures featuring CO_4^{-4} rings and chains.

At Earth's surface and in the crust, the most abundant carbonate mineral is $CaCO_3$ calcite. As with other minerals, calcite can be a rich repository of information about its environment of formation, but it is relatively underexploited in this regard. Building on their previous work on how volatile elements can be retained in calcite to provide information on ancient gas and fluid chemistry, Cherniak et al. (Chapter 10) present new results on nitrogen diffusivity in calcite. The data demonstrate that N is readily retained in calcite that does not suffer metamorphism at >500°C, or deformation, or alteration. This raises the prospects that ancient calcites could be mined for information about atmospheric evolution and the geologic nitrogen cycle.

Fe-Mg carbonates may be the most prevalent carbonate materials in the mid to lower mantle. Boulard et al. (Chapter 11) review the *sp*^{2}-*sp*^{3} structural transformation in $(Mg,Fe)CO_3$. They highlight the potential importance of Fe^{3+} carbonates: Fe disproportionation may be important to stabilizing carbonate minerals at these great depths. In addition to the change in coordination due to the *sp*^{2}-*sp*^{3} transition in carbon, Fe-Mg carbonates also exhibit an important transformation due to the spin transition of iron. Liu et al. (Chapter 12) review various experimental and theoretical methodologies in the investigation of this phenomenon and show that this transition in carbonates likely occurs between 50 and 80 GPa along the representative mantle geotherm. A substantial decrease in volume of up to 10%, shear wave splitting anisotropy, and deformation textures raise the possibility of seismic detectability. Na-Ca carbonates may also be important in certain subducted lithologies. Chapter 13 by Rashchenko et al. reviews the wide variety of crystal structures of high-pressure Na-Ca carbonates.

The daunting variety of carbonate crystal structures leads to an immensely challenging problem in working out the stable phase relations among carbonate minerals, and between carbonates and other oxides. Litasov et al. (Chapter 14) make a valiant effort to systematically evaluate the phase relations in unary, binary, and ternary carbonate systems relevant to conditions of Earth's mantle. However, phase relations in carbonate systems alone are insufficient to assess carbon phase equilibria in the mantle. Even for oxidizing conditions, the presence of additional minerals in mantle lithologies controls the distribution and nature of carbon hosts. Li et al (Chapter 15) show that at conditions of the mantle transition zone

(15 GPa and 1200°C), aragonite will react with wadsleyite in model slab lithologies to produce magnesite, Ca perovskite, and periclase. Rates of reaction are enhanced by the presence of H_2O. Because the solidus temperature of magnesite-bearing lithologies is higher, transfer of carbon from aragonite to calcite by this reaction mechanism has the effect of promoting transport of carbon deeper into the mantle.

The solubility of carbon in terrestrial magmas is a complex function of pressure, temperature, bulk composition, and oxygen fugacity. Moreover, carbon in magmas occurs in various forms. Solomatova et al. (Chapter 16) review bulk carbon solubility and the speciation of magmatic carbon based on recent insights from molecular dynamics calculations. Computational studies are especially important given the extreme challenges faced by experimentalists in inferring carbon speciation in quenched glasses, especially from very high pressure. Solomatova et al. show that molecular dynamics studies return trends in solubility and speciation that are similar to those derived experimentally, while revealing evidence for novel polymerization of carbon at very high pressures.

The solubility and speciation of carbon in high-pressure liquids is especially important for the deep carbon cycle, as melts produced from the slab afford one of the most effective ways of returning subducted carbon to the exosphere. Two chapters present new experimental results that drive home this point. Muth et al. (Chapter 17) investigated the solubility and speciation of carbon in hydrous rhyolitic melts that can be expected from sediment and slab melting along some slab-top geotherms. They find an important variation with Na number, defined as Na/(Na+K). All else equal, carbon solubility and the fraction of CO_3^{-2} relative to molecular CO_2 increase with Na number. An empirical model suggests that such melts could readily deliver the carbon found in subduction zone volcanic systems at plausible fractional contributions of slab melts to mantle wedge–derived basalts.

The low melting temperature of Ca-rich carbonated systems is highlighted by Schettino and Poli (Chapter 18). They find that model lithologies approximating pelagic limestones yield evidence for the presence of a hydrous carbonated liquid at temperatures as low as 850°C at 4.2 and 6 GPa. Such liquids would represent exceptionally efficient transport agents in subduction zone settings.

The viscosities of nominally anhydrous carbonate-rich melts at upper mantle pressures are very low, consistent with rapid ascent rates of even very small melt fractions. However, such melts are also extremely reactive and will therefore change composition upon ascent, in part by becoming more silica rich. Stagno et al. (Chapter 19) determined the viscosity of carbonate-silicate liquids at high pressure. Viscosities are about an order of magnitude higher than those of pure carbonate liquids at similar conditions, which will lead to comparatively lower ascent rates and, by virtue of increasing melt fraction, shorter residence times.

Mixtures of water and carbon dioxide are arguably the primary solvent components for fluids in the Earth's crust and upper mantle. Abramson (Chapter 20) reviews models of H_2O–CO_2 mixing behavior, informed by new data at high pressures. Though such fluids have historically been modeled as strictly molecular mixtures, phase relations and spectroscopic observations require that the topology of the miscibility gap is locally significantly impacted by reaction of CO_2 and H_2O to form bicarbonate in the fluid phase. Taking this into account poses major challenges for equations of state for mixed fluids.

Some of the carbon in crustal and mantle fluids derives from dissolution of carbonate minerals during high-pressure metamorphism, and this dissolution will be impacted by other important solutes such as alkali halides. Eguchi et al. (Chapter 21) experimentally determined calcite solubility in H_2O with varying concentrations of a range of alkali halides (NaCl, KCl, LiCl, CsCl). Rising salt concentration enhances calcite solubilty no matter the identity of the salt, but the extent of enhancement increases with decreasing ionic radius of the alkali cation.

In the experiments of Eguchi et al., the fO_2 was sufficiently high that calcite dissolution likely produced only oxidize carbonate species. However, it is increasingly being recognized that organic solutes may be important in many deep-fluid settings. Sverjensky et al. (Chapter 22) show that the chemistry of aqueous organic solutes changes profoundly with depth in the Earth. In shallow geologic fluids such as oil field brines and geothermal systems, the chemistry of aqueous organic solutes is dominated by kinetic inhibition of formation and interaction with methane. However, in deeper crustal and mantle settings, a closer approach to equilibrium predominates, which leads to aqueous species with a range of oxidation states intermediate between CH_4 and CO_2. Given appropriate conditions, phase separation to form a coexisting hydrocarbon fluid may occur.

Of the shallower environments, oceanic hydrothermal systems are especially important to aqueous organic chemistry, as they afford favorable environments for abiotic synthesis of life-essential amino acids (Ménez et al., 2018). In such settings, polypeptide synthesis is key to the formation of more complex biomolecules. Kroonblawd and Goldman (Chapter 23) performed molecular dynamics simulations to explore the pathways for aqueous glycine oligomerization at hydrothermal vent conditions. They find that relatively low temperatures of ~100°C provide optimal conditions for oligoglycine formation.

Moving deeper, one environment in which aqueous organic solutes may be much more important than previously thought is in subduction zones. Guild and Shock (Chapter 24) use thermodynamic modeling to evaluate the abundance and distribution of aqueous organic solutes in subduction zone fluids relevant to equilibration with mantle mineral assemblages. They find that organic species are important even at fO_2 of quartz-fayalite-magnetite, and become more so as fO_2 decreases. Both C1 and C2 species are stable, and their abundances increase when potential kinetic limitations on methane formation are taken into account. Canovas and Shock (Chapter 25) further explore aqueous organic chemistry during subduction, in this case with a view to evaluating the energetics of the citric acid cycle. They show that energetics may be favorable for supporting a biosphere deeper in subduction zones than previously thought. Kutcherov et al. (Chapter 26) report on experiments interpreted to have produced hydrocarbons at mantle conditions. They hypothesize a deep hydrocarbon cycle that tracks the fate of these hydrocarbons in the mantle.

Bringing things full circle, Park et al. (Chapter 27) examine the compression behavior of diamondoids, nanoclusters of sp^3 bonded carbon terminated by hydrogen. These hydrocarbon molecules, housed in a diamond-like structure, are found in natural petroleum, have potentially important material properties, and could represent an unexpected pathway to diamond growth at high pressure from subducted kerogen (e.g., Plank & Manning, 2019).

The papers in this volume represent an outgrowth of a decade of research partly stimulated by the Deep Carbon Observatory. While the past decade has seen major advances in our understanding of carbon in planetary interiors, it is clear that much remains to be done to understand the forms, transformations, and movements of carbon at extreme conditions.

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