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Why Deep Carbon?

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All chemical elements are special, but some are more special than others. Of the 88 naturally occurring, long-lived elements on Earth, carbon stands alone. As the basis of all biomolecules, no other element contributes so centrally to the wellbeing and sustainability of life on Earth, including our human species. The near-surface carbon cycle profoundly affects Earth's changeable climate, the health of ecosystems, the availability of inexpensive energy, and the resilience of the environment. No other element plays a role in so diverse an array of useful solid, liquid, and gaseous materials: food and fuels; paints and dyes; paper and plastics; abrasives and lubricants; electrical conductors and insulators; thermal conductors and insulators; ultra-strong structural materials and ultra-soft textiles; and precious stones of unmatched beauty. No other element engages in such an extraordinary range of chemical bonding environments: with oxidation states ranging from −4 to +4, carbon bonds to itself and more than 80 other elements. Carbon's chemical behavior in Earth's hidden deep interior epitomizes the dynamic processes that set apart our planet from all other known worlds.

Past consideration of the global carbon cycle has focused primarily on the atmosphere, oceans, and shallow crustal environments. A tremendous amount is known about these parts of Earth's carbon cycle. By contrast, relatively little is known about the deep carbon cycle (Fig. 1). Knowledge of the deep interior, which may contain more than 90% of Earth's carbon (Javoy 1997), is limited (Table 1). Basic questions about deep carbon are poorly constrained:

- How much carbon is stored in Earth's deep interior?
- What are the reservoirs of that carbon?
- How does carbon move among reservoirs?
- Are there significant carbon fluxes between Earth's deep interior and the surface?
- What is the nature and extent of deep microbial life?
- Are there deep abiotic sources of methane and other hydrocarbons?
- Did deep organic chemistry play a role in life's origins?

Key unanswered questions guide research on carbon in Earth. Perhaps most fundamental are questions related to understanding the physical and chemical behavior of carbon-bearing phases at extreme conditions representative of the deep interiors of Earth and other planets. We need to make an inventory of possible C-bearing minerals at pressures and temperatures to hundreds of gigapascals and thousands of degrees and we must characterize the physical and thermochemical properties of those phases at relevant pressure-temperature conditions both experimentally and theoretically (Hazen et al. 2013a, Chapter 2; Oganov et al. 2013, Chapter 3). We need to investigate the diversity of carbon minerals through more than 4.5 billion years of Earth history (Hazen et al. 2013b, Chapter 4). We must also understand the behavior of

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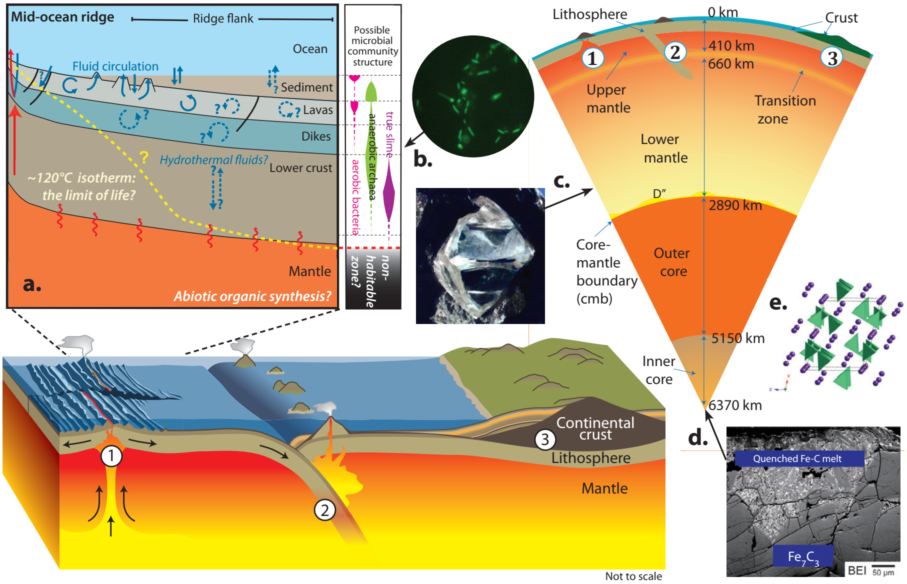

Figure 1. Earth's Deep Carbon Cycle. There is still much to learn about the cycling, behavior, and storage of Earth's deep carbon, from crust to core. Poorly quantified reservoirs of carbon include: (a) Microbial community structures on mid-ocean ridge flanks (adapted from images by Rosalind Coggon and Benoit Idlefonse). Other deep biosphere habitats affecting subsurface carbon cycling also exist. (b) An epifluorescence micrograph shows an iron-reducing enrichment culture from a serpentinite-hosted habitat. (image: Matt Schrenk). (c) Diamonds and their inclusions provide glimpses into Earth's deep interior (photo: U.S. Geological Survey). Theoretical and experimental studies allow us to speculate on carbon's role even deeper in Earth. (d) Theoretically, iron carbide (F_7C_3) is a potential constituent of Earth's solid inner core (image: Yoichi Nakajima). (e) Experimental studies suggest the existence of magnesium-iron carbon-bearing structures similar to phase II of magnesite at high pressures corresponding to depths greater than 1800 kilometers (image: Eglantine Boulard).

carbon-bearing fluids, and compile a comprehensive database of thermochemical properties and speciation of C-O-H-N fluids extending to upper mantle pressure and temperature conditions (Manning et al. 2013, Chapter 5).

The nature and extent of carbon reservoirs in Earth's deep interior is fundamental to understanding carbon in Earth. Primitive carbonaceous chondritic meteorites provide one proxy for the composition of the earliest Solar System and, by extension, Earth at the time of its formation (Marty et al. 2013, Chapter 6). However, the several weight percent carbon in those meteorites is one to two orders of magnitude greater than Earth's confirmed carbon reservoirs. What happened to the missing carbon? One key to answering this question is a comprehensive characterization of mantle carbon reservoirs and quantification of deep fluxes of carbon-bearing fluids to and from the mantle through Earth history—the essence of the deep carbon cycle (Dasgupta, 2013, Chapter 7). Current estimates of the carbon flux into Earth's mantle through tectonic subduction exceed by an order of magnitude the known carbon flux emitted by volcanoes—an untenable balance that would deplete surface reservoirs of carbon in significantly less than a billion years. Added to these uncertainties, we do not know the concentration, chemical bonding, or mineralogy of carbon in Earth's core (Wood et al. 2013, Chapter 8). Could trace amounts of carbon (a few parts per million) enter mantle silicate minerals or melts (Ni and Keppler 2013, Chapter 9)? These potential volumetrically large but diffuse carbon reservoirs contrast with such concentrated deep carbon phases as carbonate

Table 1. Possible deep carbon reservoirs

Reservoir	**Composition**	**Structure**	**[C] (mole %)**	**Depth (km)**	**Abundance (wt %)**
Diamond	C	diamond	100	>150	<< 1
Graphite	C	graphite	100	<150	<< 1
Carbides	SiC, FeC, Fe_3C	moissanite, cohenite	25-50	?	?
Carbonates	$(Ca,Mg,Fe)CO_3$	unknown	20	0 to ?	?
Metal	Fe,Ni	kamecite/awaurite	minor?	?	?
Silicates	Mg-Si-O	various	trace?	?	?
Oxides	Mg-Fe-O	various	trace?	?	?
Sulfides	Fe-S	various	trace?	?	?
Silicate melts	Mg-Si-O		trace?	?	?
CHON fluids	C-H-O-N		variable	?	?
Methane	CH_4		20	?	?
Methane clathrate	$[H_2O+CH_4]$	clathrate	variable	?	?
Hydrocarbons	C_nH_{2n+2}		variable	?	?
Organic species	C-H-O-N		variable	?	?
Deep life	C-H-O-N-P-S		variable	<15	?

Modified after Hazen et al. 2012.

magmas (Jones et al. 2013, Chapter 10) and diamonds (Shirey et al. 2013, Chapter 12), as well as volcanic emissions of carbon species (Burton et al. 2013, Chapter 11), which provide special insights to Earth's dynamic state and complex history.

Progress in all of these areas depends on the development of new instrumentation, including environmental chambers to access C-bearing samples in new regimes of *P*-*T* under controlled conditions (e.g., pH, f_{O_2}) and with increased sample volumes, as well as enhanced analytical facilities for investigating carbon-bearing samples at the nanometer scale (Mao and Boulard 2013, Chapter 13).

A central aspect of Earth's carbon cycle—one fundamentally tied to economic and environmental concerns—is the nature, sources, and evolution of subsurface organic molecules, including hydrocarbons and biomolecules. While a biologically mediated origin is postulated for most of Earth's so-called "fossil fuels," debates continue on the genesis of some deep hydrocarbons (Sephton and Hazen 2013, Chapter 14). To understand possible deep abiotic organic synthesis, including prebiotic processes that set the stage for life, we need to exploit experimental procedures to mimic deep hydrothermal geochemical environments (McCollom, Chapter 15). In this regard, a comprehensive understanding of diverse mineral-molecule nanoscale interactions at the fluid-rock interface is required (Cole et al. 2013, Chapter 16).

Any overview of carbon in Earth must assess the fascinating role of deep subsurface microbial life, which, though sparse, is widespread and thus may represent a significant fraction of Earth's total biomass. In our efforts to assess the nature and extent of the deep microbial biosphere, we are conducting a global 3-D census of deep microbial life, including both terrestrial and marine ecosystems (Colwell and D'Hondt 2013, Chapter 17). Central to any discussion of deep biology is energy flow, as exemplified by zones of serpentinization—zones of intense hydrogen production that possibly represent the oldest ecosystem on Earth (Schrenk et al. 2013, Chapter 18). Any understanding of the nature and survival of deep life entails investigations of biomolecular adaptations under extreme conditions, which in turn necessitates a new laboratory-based approach to studying life at extreme pressures and temperatures (Meersman et al. 2013, Chapter 19). Most enigmatic of all are deep viruses, which promote rapid microbial turnover rates and lateral gene transfer and thus may play the dominant role in evolution of subsurface ecosystems (Anderson et al. 2013, Chapter 20).

FRONTIERS OF DEEP CARBON RESEARCH

Carbon in Earth represents a synthesis of a diverse body of research in physics, chemistry, biology, and the Earth and space sciences. The richness of this collection points to the potential for new discoveries, as the findings in one scientific domain often inform those in another seemingly unrelated field. (Indeed, one colleague has suggested that we should have the authors read the entire volume and then start writing their chapters over again!)

One example illustrates this kind of potential cross-fertilization. In Chapter 4, Hazen et al. (2013) point to dramatic changes in Earth's near-surface carbon mineralogy through more than 4 billion years of Earth history. The innovation of carbonate biomineralization and the rise of the terrestrial biosphere, in particular, have increased the crustal diversity, volume, and distribution of carbon-bearing minerals and other substances. In Chapter 3, Oganov et al (2013) consider high-pressure carbon-bearing minerals, including those in Earth's mantle and core. In Chapter 7, Dasgupta (2013) argues that the upper mantle geotherm of the past billion years is sufficiently cool for subducted carbonates to remain largely sequestered in the mantle—a situation that contrasts with prior eons of Earth history. And in Chapter 11, Burton et al. (2013) catalog all known volcanic emissions of carbon and conclude that these varied sources collectively represent only a small fraction of the carbon that is being subducted. Taken together, these observations suggest a possibly dramatic Phanerozoic increase in the amount of subducted carbon that remains sequestered in the mantle—a trend that could lead to significant depletion of crustal carbon, and thus adverse biological consequences, within a few hundred million years. Further research is needed to evaluate the extent to which life might contribute to its own demise by contributing to a net transfer of carbon from the crust to the mantle. Similar insights await the thoughtful and diligent reader of this volume.

Carbon in Earth, though extensive, is by no means encyclopedic and significant swaths of Earth's carbon story are missing from these pages. For example, we all but neglect the nature and origins of coal—one of the crust's most concentrated and extensive carbon reservoirs (see, however, Manning et al. 2013). In spite of a once-thriving research community (Van Krevelen 1993; Davidson 2004; and references therein), and coal's continuing economic importance and environmental implications, research on this fascinating substance has all but ceased. Details of coal's structural chemistry and complex maturation processes remain obscure, and thus represent a promising potential direction for future research on carbon in Earth.

Similarly missing is a comprehensive treatment of non-volcanic fluxes of deep carbon, including deep crustal sources and sinks. On the one hand, significant CO_2 is released through regional metamorphism of carbonate-rich sedimentary sequences (Bowen 1940; Ferry 1992; Kerrick and Caldeira 1993, 1998; Bickle 1996; Ague 2000, 2012). On the other hand, retrograde metamorphism may be a sink for CO_2. Research on retrograde metamorphism is key for understanding whether or not fluids transport significant CO_2 from the deep crust to the shallow hydrosphere and atmosphere. In some deep crustal zones CO_2-rich fluids may drive dehydration reactions—the process of charnockitization—and contribute to the stabilization of continental cratons (Janardhanan et al. 1979; Newton et al. 1980). The net effects of these metamorphic processes on the carbon cycle today, not to mention their variations through Earth history, are not well understood.

Several chapters in this volume allude to the central roles played by plate tectonics in Earth's carbon cycle, notably in subduction zones (e.g., Daspgupta 2013) and back-arc and ridge volcanism (Burton et al. 2013; Jones et al. 2013). Nevertheless, important aspects of large-scale geodynamics and geophysical modeling are lacking from *Carbon in Earth*. For example, although Shirey et al. (2013) present remarkable data on diamond inclusions that may point to the start of modern-style lateral tectonics and the Wilson cycle approximately 3 billion years ago, subsequent effects of the "supercontinent cycle" on the carbon cycle through deep time are not well understood. Nor do our models of carbon cycling yet incorporate the impacts of episodic megavolcanism associated with massive flood basalts—events that correlate with several intervals of Phanerozoic mass extinctions, and thus must have affected the distribution of crustal carbon. And we have yet to bring to bear the full geophysical arsenal of techniques to probe the nature and distribution of carbon-bearing solid and fluids in Earth's deep interior.

Other telling gaps in our knowledge of deep carbon relate to the fascinating deep biosphere. Remarkable discoveries of subsurface microbial life (Colwell and D'Hondt 2013) and associated viruses (Anderson et al. 2013) hint at a surprising hidden diversity, primarily within the microbial domains of archaea and bacteria. However, as Colwell and D'Hondt (2013) point out, surprising discoveries of a rich subsurface community of eukayotes promises an even richer deep taxonomy (Monastersky 2012; Orsi et al. 2012). These findings, coupled with advances in single-cell genomics (Stepanauskas and Sieracki 2007; Stepanauskas et al. 2012), predict a coming decade of extraordinary discovery.

At this stage in our pursuit of a fundamental understanding of carbon in Earth, our knowledge baseline as set forth in the following chapters is significant, but the unanswered questions—what we know we don't know—far outweigh what we know. That's an energizing state for any scientific pursuit, for the unknown is what beckons us to the laboratory, the field, and the computer.

And yet, as we embark on this decadal quest, the greatest lure is not so much the assurance that we will fill in many gaps in what we know we don't know, but rather that we will discover entirely new, unanticipated phenomena. Even though we are unable to articulate what those discoveries might be, we can be assured that such adventures lie in wait for the curious and prepared mind.

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