

# Paleontology of Earth's Mantle

Norman H. Sleep,<sup>1</sup> Dennis K. Bird,<sup>2</sup> and Emily Pope<sup>2</sup>

<sup>1</sup>Department of Geophysics and <sup>2</sup>Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305; email: norm@stanford.edu

Annu. Rev. Earth Planet. Sci. 2012. 40:277–300

First published online as a Review in Advance on January 30, 2012

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

This article's doi:  
10.1146/annurev-earth-092611-090602

Copyright © 2012 by Annual Reviews.  
All rights reserved

0084-6597/12/0530-0277\$20.00

## Keywords

Hadean, Archean, anoxygenic photosynthesis, kimberlite, carbonatite, serpentine, zircon, Gaia, nitrogen

## Abstract

Solid, liquid, and gaseous products of life's metabolic processes have a profound effect on the chemistry of Earth and its fluid envelopes. Earth's mantle has been modified by the ubiquitous influence of life on recycled lithosphere, with dramatic changes resulting from subduction of redox-sensitive minerals following the rise of photosynthetic oxygen approximately 2.5 billion years ago. Throughout geological time, production and degradation of organic carbon affected minor-element, trace-element, and isotopic systems in the mantle. Carbon in the mantle decreased as carbonate sediments sequestered CO<sub>2</sub>, but nitrogen concentrations were augmented by subduction of biologically derived ammonium structurally bound in diagenetic minerals. The biologically modulated mantle vents its biosignatures through island arc and oceanic volcanoes, with fractionated sulfur isotopes providing a durable record. Deeply subducted CO<sub>2</sub>-rich domains are the source of carbonatite melts, as well as eclogitic diamonds with low <sup>13</sup>C/<sup>12</sup>C ratios and remnant biologically derived nitrogen. The mantle preserves a concentrated biological record throughout Earth history, thus giving expectation of finding a Hadean record of life.

## INTRODUCTION

Abundant photosynthetic life appears to have colonized Earth by  $\sim 3.8$  billion years ago (Gya). Highly metamorphosed black shales and banded iron formations with seawater-like signatures and remnants of ancient life are documented in the oldest known sequences of supercrustal rocks (Mojzsis et al. 1996, Nutman et al. 1997, Rosing 1999, Rosing & Frei 2004, Dauphas et al. 2007, Friend et al. 2008, Nutman et al. 2009, Papineau et al. 2010, Pons et al. 2011). Graphitic carbon (C) in these units is depleted in  $^{13}\text{C}$  relative to  $^{12}\text{C}$  (expressed as negative  $\delta^{13}\text{C}$ ); these isotopic ratios are similar to those of known products of biological carbon fixation by photosynthesis (e.g., Thomazo et al. 2009). However, the terrestrial geologic record before  $\sim 3.8$  Gya is meager, consisting of ancient zircon crystals eroded from their parent rocks and then deposited in younger sediments (e.g., Harrison 2009), highly metamorphosed mid-crustal igneous rocks (e.g., Bowring & Williams 1999), remelted components of ancient rocks preserved in younger igneous rocks (Iizuka et al. 2009, Upadhyay et al. 2009), and similar chemical signatures possibly derived from protocrust of Hadean age in younger volcanosedimentary rocks (Tessalina et al. 2010).

Given this dearth of data, we address two parallel issues that expand on a short discussion presented by Sleep (2010). First, the effects of photosynthesis on extant crystalline rocks are profound; one cannot blindly extrapolate current conditions back into prebiotic time. Second, in spite of this, Earth's mantle and crystalline basement may sequester an unexploited Hadean paleontological record of last resort. As an example of pervasive biological effects, photosynthesis harvests solar energy into geochemical cycles by oxidizing Earth's fluid envelopes and the crustal rocks of the continents and ocean floor with which these fluids interact (Lecuyer & Ricard 1999, Rosing et al. 2006). Biological processes, especially those within oxidized environments, which arose from photosynthesis at the Archean-Proterozoic transition, contribute directly or indirectly to the occurrence of most of the 4,300–4,400 known mineral species (Hazen et al. 2008, Papineau 2010). Many of the organisms that use minerals as substrates utilize oxidants from photosynthesis (see table 1 of Shock 2009). Still, some modern life persists independently of photosynthetic life (e.g., Nealson et al. 2005) deep in crustal rocks, at hydrothermal vents near the surface and at the bottoms of ocean basins, and in sediments. Nevertheless, products of photosynthesis are ubiquitous in the environments of all modern terrestrial organisms.

The study of Hadean prebiotic environments is analogous to attempts by archaeologists and ecologists to infer prehuman conditions in North America. The question of whether the vast extent of tall grass prairie in the central United States was made by humans arose soon after the Native Americans were evicted (Harvey 1908a,b). Other human-made environments in putative wilderness regions are still being recognized. The "typical" meandering stream in the eastern United States occupies an abandoned millpond (Walter & Merritts 2008). Oak-hickory and beech-maple forests in the same region were products of conscious forest management by the Native Americans (Abrams & Nowacki 2008). Broad-leaf trees became much more abundant and spruce became uncommon once early Americans exterminated the Pleistocene megafauna (Gill et al. 2009). Nevle et al. (2011) discussed global changes in atmospheric composition and climate associated with reforestation following European conquest of the Americas.

Similarly, in this review, we first illustrate the pervasive nature of biological effects on large geochemical reservoirs by considering the oxidation of Earth's crust. We then evaluate evidence for Archean and later biological influence on the mantle. Finally, we identify geological environments in modern Earth that owe their existences to biochemical processes, and we identify ideal candidate environments that might preserve a Hadean record of both prebiological chemical signatures and the emergence of biologically mediated geochemical processes.

## OXIDATION OF THE CRUST

The oxidation of Earth's crust is an example of the measurable effect that waste products of biological activity have on crystalline rocks in the crust. This discussion serves to introduce widespread geochemical processes that, through subduction of surface material (discussed in the next section), have likely affected the mantle. Beginning with mass-balance constraints, we note that Earth's crust is strongly oxidized relative to possible mantle source rocks. Bookkeeping requires attention to carbon, sulfur, and iron, which have multiple accessible oxidation states and sufficient abundances in Earth's crust to act as crustal reservoirs for available oxygen. The oxidation states of these elements in mantle-derived igneous rocks, the ultimate sources of the crust, provide a convenient frame of reference. Volcanic carbon is dominantly in the form of CO<sub>2</sub>, and volcanic sulfur is sulfide (SO<sub>2</sub> gas and elemental brimstone sulfur form at shallow levels; Witter et al. 2005). Iron is dominantly Fe(II) in all mantle phases.

Below, we review the global mass balance of these crustal, redox-sensitive major elements. In addition, trace-element ratios in rocks retain durable information about surface redox conditions that later alteration—for example, oxidation of Fe(II) to Fe(III)—may obscure in the major elements. We discuss uranium/thorium (U/Th) crustal ratios and lead (Pb) isotopes as durable examples to introduce the application of trace-element methods to the evaluation of the effects of life's metabolic processes on the chemistry of the mantle.

### Global Mass Balance of Crustal Oxidants and Reductants

Iron and sulfur in lavas are immobile at seafloor pressures, so their concentrations can be measured (e.g., Krauskopf & Bird 1995). Basalt, komatiite, and serpentinite are approximately 10% FeO by mass. Andesite from arc volcanoes has ~7% FeO. In contrast, sulfide is typically present in minor amounts: There is approximately 0.1% sulfur in basalt. Manganese is the next most abundant element in terms of mol equivalent O<sub>2</sub> with multiple available oxidation states; its concentration (0.18% MnO in basalt; e.g., Krauskopf & Bird 1995) has slight effects on the global oxygen budget that we ignore.

Earth's atmosphere is an obvious but a modest reservoir of available oxygen ( $38 \times 10^{18}$  mol); marine sulfate ( $80 \times 10^{18}$  mol equivalent O<sub>2</sub>) and sedimentary sulfate ( $280 \times 10^{18}$  mol equivalent O<sub>2</sub>) are well constrained (Holser et al. 1988). The principal reservoir for Fe(III) consists of crystalline metamorphic and igneous rocks in the continental crust. However, a primary uncertainty in evaluating mass-balance constraints for Fe(III) is the equivalent thickness of oxidized crust. We assume that the crust is well mixed by tectonics over geological time, so the thickness is crudely the crustal thickness, 30 to 40 km. This reasoning yields a reservoir of  $2,000 \times 10^{18}$  mol equivalent O<sub>2</sub> (Lecuyer & Ricard 1999). Sedimentary Fe<sub>2</sub>O<sub>3</sub>-bearing rocks, including banded iron formations, are much smaller reservoirs of excess oxygen (Holser et al. 1988).

The available oxygen reservoirs are products of photosynthesis that initially left complementary reservoirs of reduced carbon. The familiar form of oxygenic photosynthesis produces O<sub>2</sub>. Fe(III) and sulfate are produced indirectly by the oxidation of Fe(II), and sulfide by O<sub>2</sub>. Anoxygenic photosynthesis directly produces Fe(III) from Fe(II) and sulfate from sulfide. Thus, significant buried organic carbon, sulfate, and Fe(III) could have accumulated on the early Earth before oxygenic photosynthesis evolved.

Notably, the equivalent sum of the available oxygen reservoirs ( $2,400 \times 10^{18}$  mol) is twice the "visible" complementary reduced reservoir of carbon, which consists of buried carbon from photosynthesis ( $1,200 \times 10^{18}$  mol; Holser et al. 1988). One must thus postulate a "hidden" reduced reservoir. Subduction of organic-rich black shales in excess of subducted oxidants is one possibility.

Catling et al. (2001) suggest that the hydrogen in methane from photosynthesis escaped to space. Water is the ultimate source of the hydrogen, so the net effect is to reduce Earth's water inventory and to augment the oxygen in the crust. The mechanism occurred only before there was free O<sub>2</sub> in the air and did not require oxygenic photosynthesis.

### Trace-Element Ratios: Uranium-Thorium Fractionation

Oxidation of Earth's crust repartitions redox-sensitive trace elements. The system of uranium (U), thorium (Th), and lead (Pb) isotopes conveniently provides age as well as redox information. Uranium occurs as U(IV) and thorium as Th(IV) in mantle-derived igneous rocks. These oxidation states are insoluble in water, so U/Th changes little during weathering, crustal metamorphism, and hydrothermal alteration in anoxic conditions. Uranium becomes the soluble species U(VI) under oxic conditions, whereas thorium remains Th(IV). Lead isotopes provide a durable record of this fractionation and hence oxic environments: <sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th decay to <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb with half-lives of 4.51, 0.704, and 14.05 billion years (Ga), respectively. A rock can become enriched in <sup>207</sup>Pb relative to the other lead isotopes only early in the history of Earth.

Rosing & Frei (2004) detected this <sup>207</sup>Pb enrichment in ancient ~3.7-Ga-old metamorphosed sediments in West Greenland. The straightforward explanation is that dioxygen-producing photosynthetic organisms had evolved by then. O<sub>2</sub> reacted with U(IV) in weathered rocks, producing soluble U(VI) that was transported into a marine organic-carbon-rich mudstone environment, where U(VI) was reduced to immobile U(IV). Thorium in the weathered rocks did not become soluble. The observed significant excess of <sup>207</sup>Pb relative to <sup>208</sup>Pb indicates that the U(VI) mobilization occurred early in Earth's history, when significant <sup>235</sup>U persisted. This hypothesis, however, does not imply that there was significant oxygen in the air. Oxygen, like methane in a modern swamp, is weakly soluble and can build up quickly to saturation in poorly aerated water, and it dissipates through reactions with the ambient rock.

It is conceivable that U(VI) formed indirectly when ferric iron or sulfate oxidized U(IV). Ferric iron and sulfate were likely available as products of photosynthesis and of purely abiotic processes. Regarding abiotic processes, the oxidation of U(IV) to U(VI) is allowed thermodynamically in weakly oxidizing conditions where no dioxygen is present (figure 7 of Harrison 2009). The reduction of Fe(III) to Fe(II) abiotically oxidizes U(IV) to U(VI) (D.R. Lovley, personal communication, 2011). Thus, the environmental geochemistry of uranium is a model-dependent durable biosignature on the very early Earth. As a measure of current ignorance, poorly characterized uranium-bearing cellular compounds (Cvetkovic et al. 2010) and arsenite-based photosynthesis (Kulp et al. 2008) have recently been discovered.

Plutonium is another potential early Earth biosignature, as significant plutonium still existed on the Hadean Earth. Weakly oxidized environments associated with biological processes conceivably fractionated uranium relative to plutonium. It is warranted to examine Hadean zircons for evidence of this process. Turner et al. (2007) found no evidence of significant fractionation. Harrison (2009) interpreted zircon data to imply that fractionation did occur.

### MANTLE RECORD OF POST-HADEAN ENVIRONMENTS

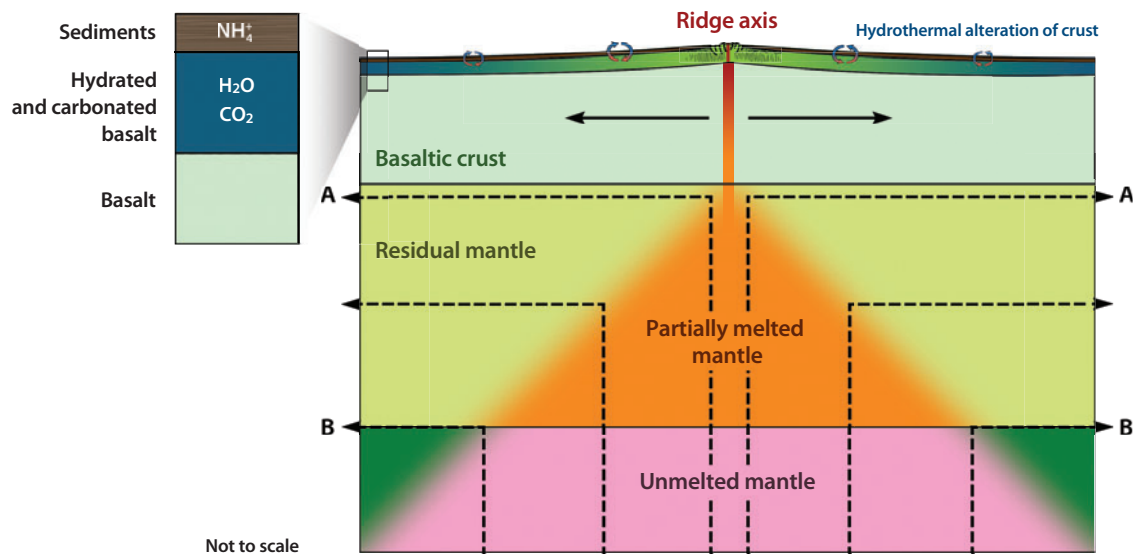
The mantle and ancient mantle-derived igneous rocks within the continental crust conceivably retain Hadean biological information. An example would be biologically mediated chemical signatures, such as those described above, preserved within zircon crystals eroded from Hadean crystalline basement rocks and deposited in younger sediments. To demonstrate the feasibility of Hadean mantle paleontology, we review numerous published studies describing examples in

which the mantle preserves biological information from Archean and younger times. Subducted heterogeneous domains sequester a paleontological record revealed in isotopic and trace-element variations in subsequent mantle-derived igneous rocks. Furthermore, the effects of biology on the mantle are pervasive enough to modify the gross concentration of biologically important elements—including carbon, nitrogen, and possibly phosphorus (which we do not consider)—over geological time.

We provide an overview of plate processes and mass balances of relevant elements. Then we begin our discussion about global mantle processes with carbon, as it provides an easily studied durable mantle record of surface processes and is the clearest example of the effects of biology on mantle geochemistry. Photosynthesis has strong effects on the redox state and sulfur concentration of arc volcanics, highlighting a mantle composition in which subduction of the surface reservoirs (discussed in the previous section) is obvious.

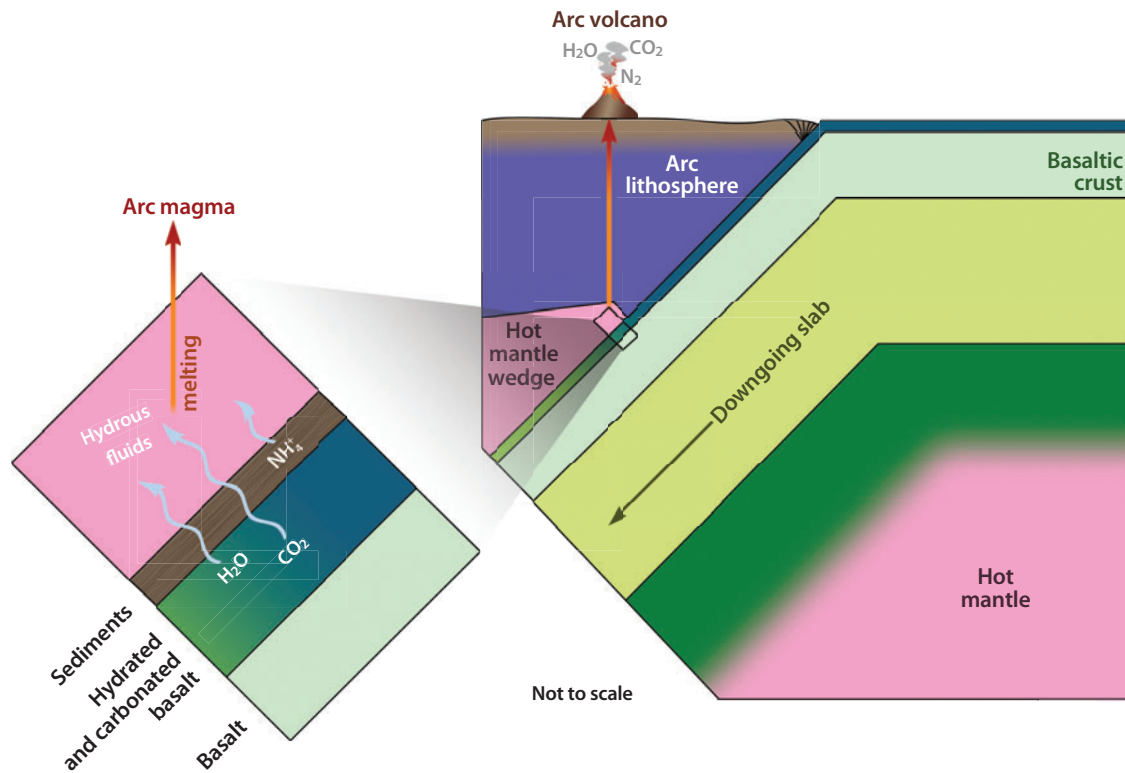
## Global Plate Processes

Plate tectonics caused the mantle to become heterogeneous over geological time. It has repeatedly destroyed and exhumed heterogeneities. We begin discussion of the mantle cycle with ridge axes, where upwelling material partially melts (**Figure 1**) and magma ascends to form the basaltic oceanic crust. The melts pond and mix in the axial magma chamber, especially at full spreading rates of  $>60 \text{ mm year}^{-1}$ . Mixing obscures the chemical and isotopic nature of the individual melted domains. Hydrothermal circulation exchanges material between the ocean and the oceanic



**Figure 1**

Schematic diagram of ridge axis. Material partially melts as it ascends. Path A melts extensively, freezing to depleted residuum just beneath the crust. Path B just reaches the depth of partial melting. The basaltic oceanic crust is the pooled product of these melts. It is underlain by the olivine-rich residue from the melting and unmelted mantle. The permeable uppermost  $\sim 0.5 \text{ km}$  of the oceanic crust reacted with  $\text{CO}_2$  in warm (tens of degrees Celsius) seawater to form carbonates while the crust was less than  $\sim 1$  million years old. Sediments, including organic-carbon-rich layers, cover the basalt. The basaltic crust is currently  $\sim 6 \text{ km}$  thick, and the depleted residual layer is  $\sim 50 \text{ km}$  thick. There was more melting on the early Earth, as the mantle was hotter. The crust could have been  $25 \text{ km}$  thick and the residual layer,  $100 \text{ km}$  thick.



**Figure 2**

Schematic diagram of subduction zone. The slab carries the oceanic crust and its underlying lithospheric mantle into the deep interior. The uppermost basaltic crust is carbonatized and hydrated near the ridge axis by reactions with seaway-derived hydrothermal fluids, producing secondary carbonate and hydrous minerals. Hydrous and carbonate minerals are also present in the sediments. Ammonium is present in organic-carbon-rich sediments. During subduction, the hot overlying mantle heats the sediments and basaltic material; this causes hydrous minerals to become unstable, liberating water. The water lowers the melting point in the mantle, and hydrous magma ascends to the surface at the island arc. Some nitrogen and  $\text{CO}_2$  escape from the slab in this process. Subducted material rarely melts on the modern Earth but did melt more frequently on the ancient Earth, when the mantle was hotter. Earth did not become habitable until its interior was cool enough that  $\text{CO}_2$  remained in carbonatized basalt. The subducted material types retain their chemical identities and are distinct domains for subsequent melting.

crust. This process, over geological time, has buffered the composition of the ocean. Analysis of rare-earth elements and yttrium (Y) in metamorphosed banded iron formations precipitated from seawater indicates that this process has maintained seawater at its modern pH of  $\sim 8$  since at least 3.85 Gya (Friend et al. 2008). Prebiotic and Archean seawater differed from modern seawater in that  $\text{O}_2$  was not present and there was much less dissolved sulfate.

Sediments accumulate on the exposed crust as it moves away from the ridge. Weathering of landmasses is the source of marine sediment deposits, including the oxidized and reduced products of terrestrial photosynthesis. Subduction then entrains vast quantities of marine surface material into the mantle, including oxidized and organic products of terrestrial and marine photosynthesis (Figure 2). The stratified domains of the oceanic lithosphere—basaltic crust, depleted mantle residuum, and unmelted mantle—retain much of their chemical identity during subduction. Subducted sediments and the uppermost oceanic crust dehydrate as they encounter hot mantle. The



hydrous fluid formed by this process ascends into the hot mantle wedge, where its presence lowers the melting temperature of the mantle, forming arc magmas. Biologically modified materials carried by the oceanic crust may alternatively be directly accreted to arcs and continents, be trapped within the mantle wedge, or continue down into the deep mantle with the subducting slab. The latter fate leaves a long-lasting signature that can be observed when mantle flow returns the material as mantle xenoliths, components in igneous rocks, and rocks exhumed by tectonic processes.

Subduction has a direct control on the concentration of water in the mantle. Any subducted water must pass through the dehydration and melting zones. Melting in the mantle wedge continues until water is depleted to the concentration at which it no longer affects melting. Over geological time, most of the mantle, at some point, has cycled downward through the melting zones of island arcs and then continued down with the slab. The bulk mantle thus holds a critical concentration of water to affect melting beneath the arc. Arc volcanism returns the remaining water to surface reservoirs, including the ocean. Some carbon, nitrogen, and sulfur along with numerous trace elements also enter the hydrous fluid from the slab and become components of arc magmas. Albarède (2009) reviewed evidence for water in Earth's mantle on the basis of similar water/ cerium ratios in mantle-derived mid-ocean ridge basalts and ocean island basalts. His estimate of water in the mantle, 150–350 parts per million (ppm), is compatible with the concept that water is at the minor-major element threshold. This concentration is equivalent to 0.45–1.07 ocean masses, extrapolated to the whole mantle. Albarède (2009) gave the caveat that hydrous phases and water in nominally anhydrous minerals are stable throughout much of the mantle, so that a massive “hidden” mantle water reservoir is possible provided it does not circulate through volcanic source regions.

## Global Mantle Carbon Cycle

The sequestration of CO<sub>2</sub> into rocks during the Hadean was a necessary condition for the surface of Earth to become habitable (Sleep et al. 2011). There is considerable potential for a durable prebiotic record, as three-quarters of Earth's CO<sub>2</sub> needed to subduct before its surface was habitable even by thermophilic organisms (Sleep et al. 2001, Zahnle et al. 2007). One would expect little carbon isotopic fractionation under these abiotic conditions.

In the context of plate tectonics (Sleep 2009), the ridge is both a source and a sink of CO<sub>2</sub>. Carbon dioxide is essentially insoluble in crystallizing basaltic magmas at the low pressures of the oceanic crust. Hot (~350°C) black smoker vents carry magmatic CO<sub>2</sub> into the ocean. Off-axis (until a crustal age of ~1 million years), warm (tens of degrees Celsius) hydrothermal circulation carries CO<sub>2</sub>-bearing seawater into the permeable uppermost ~0.5 km of the basaltic crust. Here, CO<sub>2</sub> is sequestered into carbonate minerals by reaction with the basaltic crust and is thus quantitatively depleted from hydrothermal vent water. The hydrothermal flux of CO<sub>2</sub> from the ocean to the basalt is thus proportional to the total CO<sub>2</sub> concentration in the ocean, and the net effect buffers CO<sub>2</sub> concentrations in the ocean and atmosphere. Nakamura & Kato (2004) and Shibuya et al. (2007) studied ~3.46-Ga-old carbonatized oceanic crust from Australia, showing the minimum antiquity of the process. There is some evidence of carbonatized oceanic crust in highly metamorphosed ~3.8-Ga-old exposures in Greenland (Friend et al. 2008).

Subduction of carbonatized oceanic crust and sediments creates domains that are highly enriched in carbon relative to average mantle. We can obtain a factor-of-a-few estimate of relative enrichment by assuming that the degassing of CO<sub>2</sub> at the ridge axis balances the sequestration of CO<sub>2</sub> in carbonates of altered oceanic crust. The degassed CO<sub>2</sub> comes from the melted region beneath the ridge axis, which has a modern thickness of ~50 km (**Figure 1**; see also Plank & Langmuir 1992). The carbonatized oceanic crust is ~0.5 km thick, giving a relative CO<sub>2</sub>

concentration  $\sim 100$  times that of the bulk mantle. Subducted sediments also host reduced carbon-rich domains resulting from primary production of photosynthetic organisms. Both types of subducted domains—carbonatized oceanic crust and carbon-rich sediments—melt to form  $\text{CO}_2$ -rich magmas, which recognizably return to the surface within magmas at modern island arcs and elsewhere within kimberlites (diamond pipes) and carbonatites. Observations by Walter et al. (2011) confirm the reality of subduction of shallow oceanic crust and organic-rich sediments into the lower mantle and hence the mantle-wide convection that we assume in our mass balances. They described mineral inclusions in diamonds with isotopic and chemical composition appropriate for subducted oceanic crust and sediments. The inclusions crystallized at lower mantle pressures before the mantle source region partially melted at shallower depths to form kimberlite.

In modern arc environments, carbon isotopes and  $^3\text{He}$ , which is present in significant amounts only in the mantle wedge, can be used to determine the relative fraction of volcanic  $\text{CO}_2$  that is mantle-derived or that comes from subducted sediments and organic material (Sano & Williams 1996). However, only carbon isotopes leave a durable record in older lavas, as rocks do not retain He during metamorphism. Song et al. (2009) recognized the presence of reduced organic carbon exhumed by tectonics from the melting zone of an island arc using  $^{13}\text{C}$  and the presence of  $\text{CH}_4$  in exposed mantle rock. They noted that the partition of trace elements into a melt from mantle that has been metasomatized by reduced fluids from subducted sediments should differ from that in mantle that was metasomatized by an oxidized,  $\text{CO}_2$ -rich fluid derived from carbonatized crust. Thus, there are potentially trace-element markers of the subduction of organic carbon in ancient arc-related igneous rocks. Foley (2011) discussed the redox states of subducted domains and the effects of redox reactions on mantle melting. He suggested that examination of mantle-derived lavas would further quantify the variations in subducted material over geological time.

With time, biology has strongly affected the partitioning of carbon between surface and mantle reservoirs, as extensive sedimentary carbonate deposits on stable continental platforms are a product of photosynthesis and do not subduct. These types of carbonate rocks appeared relatively late in Earth's history. The Steep Rock sequence in Ontario, at 2.78 Ga old, is probably the oldest known example (Stone 2010). Limestone deposition in shallow platform environments requires at least locally oxic water with low Fe(II) concentration, as Fe(II) kinetically inhibits calcite formation (Sumner & Grotzinger 1996, Kamber 2010). Nisbet et al. (2007) interpreted carbon isotopic evidence of oxygenic photosynthesis at the geological time of the Steep Rock stromatolites in Ontario, Canada.

Once  $\text{CO}_2$  is sequestered in platform carbonates, chemical weathering can mobilize  $\text{Ca}^{2+}$  with  $2\text{HCO}_3^-$ . However, the calcium carbonate simply precipitates elsewhere in the crust, and the net effect is only the relocation of the limestone deposit from one place to another. Platform carbonates therefore act as a bucket trap for  $\text{CO}_2$ , in which the globally available divalent cations and sedimentary platform environments delimit a specific amount of carbonates. The mantle receives the remaining available  $\text{CO}_2$  in the form of subducted carbonatized oceanic crust.

Mass-balance relationships indicate that platform carbonates have a significant global effect on mantle composition. Estimates of sedimentary carbon are  $7,100 \times 10^{18}$  mol (Holser et al. 1988) to  $7,750 \times 10^{18}$  mol (Hirschmann & Dasgupta 2009), equivalent to  $\sim 62$ – $68$  bars of atmospheric  $\text{CO}_2$ , respectively. Of this volume, 15–20% by mol is organic carbon, and the remaining 80–85% is carbonate (Holser et al. 1988). Hirschmann & Dasgupta (2009) have critically reviewed published estimates of  $\text{CO}_2$  in the mantle, giving a range of  $\sim 9,750 \pm 4,200 \times 10^{18}$  mol, with the center equivalent to  $\sim 85$  bars of atmospheric  $\text{CO}_2$ . The continental lithosphere may represent another carbon reservoir owing to intrusions of kimberlites at its base over geological time. This poorly constrained reservoir contains  $\sim 5,000 \times 10^{18}$  mol, equivalent to  $\sim 43$  bars of atmospheric pressure (Sleep 2009).



Platform carbonates are also a key component of the well-known climate Urey buffer. Metamorphism of  $\text{SiO}_2$  and carbonate forms new minerals containing  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$  and returns a continual flux of  $\text{CO}_2$  to the ocean and air. The weathering rate of silicate rocks increases with climatic temperature and biological activity. Weathering supplies the surface system with divalent cations that quickly enter the ocean and form platform carbonates, maintaining a buffered  $\text{CO}_2$  atmosphere. Over geological time, platform carbonates act as a trap for  $\text{Ca(II)}$  as well as  $\text{CO}_2$ . There is approximately twice as much  $\text{Ca(II)}$  in global sedimentary rocks than could have come from any reasonable mixture of igneous source rocks (Sibley & Vogel 1976). Hydrothermal vents at ridge axes are the obvious source of the element.

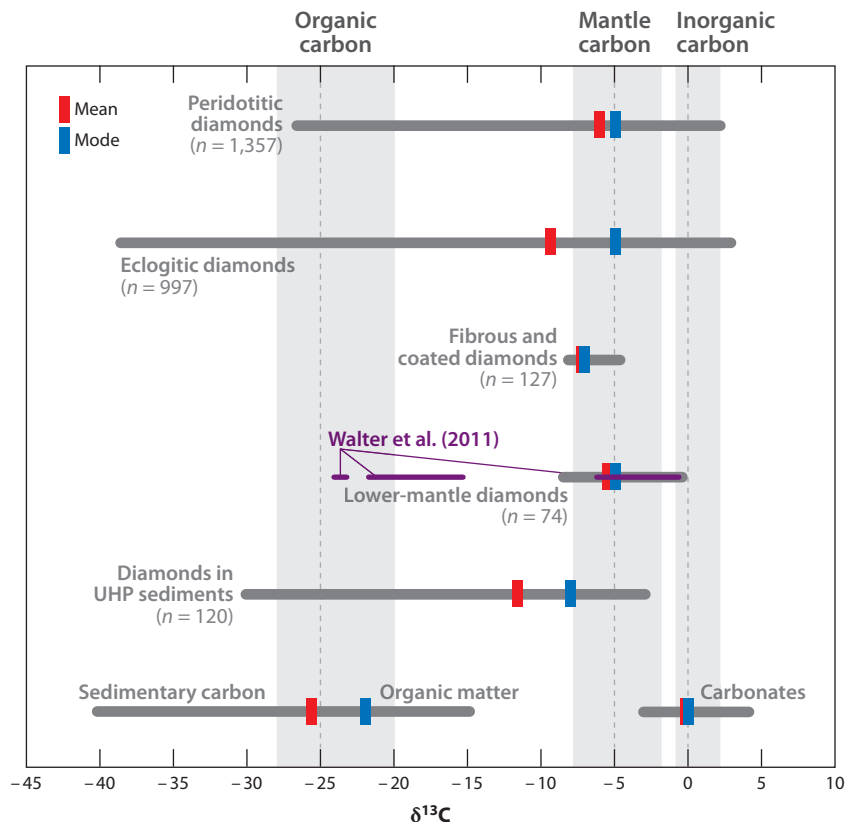
The Urey buffer can dominate only if the total  $\text{CO}_2$  concentration in seawater is low enough that the flux from carbonatization of the oceanic crust is less than the flux of  $\text{CO}_2$  into sediments. This situation is likely at present (Caldeira 1995). Conversely, the ocean crust as a sink for  $\text{CO}_2$  likely dominated on the early Earth (Sleep & Zahnle 2001). By this reasoning, the  $\text{CO}_2$  concentration in the atmosphere and ocean decreased until the Urey buffer became dominant. That is, oxygenic photosynthesis, by producing an alternative  $\text{CO}_2$  sink, acted as an indirect control on the rate at which  $\text{CO}_2$  subducts in the mantle.

We note that pelagic microbes now precipitate large quantities of  $\text{CaCO}_3$  on the open seafloor. This biological activity became significant only in the past  $\sim 150$  million years (Sibley & Vogel 1976) and presents a potentially major future biological effect on Earth's mantle. Little of this carbonate has reached subduction zones thus far (Plank & Langmuir 1998). Therefore, whether these deposits will be subducted into the mantle or obducted into the accretionary wedge is unclear. As an example, the Cuban arc provides good exposure of large deposits of accreted seafloor carbonates (Saura et al. 2008).

When  $\text{CO}_2$ -rich domains are subducted, they often retain their chemical and isotopic identities, as solid-state chemical diffusion is extremely slow. They represent the first significant material to melt in ascending mantle beneath mid-ocean ridges and within mantle plumes (Dasgupta & Hirschmann 2007, Francis & Patterson 2009). Dixon et al. (2008) recognized this  $\text{CO}_2$ -rich material as a component of rejuvenated late-stage Hawaiian lavas. Variations in the fraction of  $\text{CO}_2$ -rich magma in the erupted mixture at mid-ocean ridges have produced observable heterogeneity in the ratio of  $\text{CO}_2$  to trace elements, including niobium (Nb) (Donnelly et al. 2004, Dasgupta et al. 2009).

The oldest evidence of  $\text{CO}_2$  subduction comes from alkaline magmas intruded in India at  $\sim 1.48$  Gya (Upadhyay et al. 2009). Analysis of whole-rock  $^{142}\text{Nd}/^{144}\text{Nd}$  shows the signature of a  $\sim 4.2$ -Ga-old mantle reservoir in the magma source region, which we associate with formation and subduction of carbonate-altered seafloor. The material circulated through the mantle, melted, and intruded the Indian lithosphere at  $\sim 3.6$  Gya, according to  $^{207}\text{Pb}/^{204}\text{Pb}$  measurements and the craton age. It remelted and ascended to the surface at  $\sim 1.48$  Gya. There is no reported carbon isotope data on these rocks that would support whether photosynthesis occurred at the time of subduction, but these observations suggest that there is some hope of finding more rocks with Hadean subduction source ages. Several Archean carbonatites and kimberlites have been discovered (Rukhlov & Bell 2010), the oldest of which is the  $\sim 3.0$ -Ga-old Tupertalik complex in Greenland (Bizzarro et al. 2002).

Kimberlites that have erupted through the continental lithosphere provide information on subducted domains, although these magmas interacted extensively with the mantle lithosphere during their ascents from their source regions and underwent assimilation and fractional crystallization (Francis & Patterson 2009). Later thermal events remobilized the material that had intruded into the deep lithosphere (Tappe et al. 2008). The net effect of melting and freezing is the movement of  $\text{CO}_2$ -rich material from basalt-hosted domains in subducted oceanic crust to



**Figure 3**

Ranges (*horizontal gray bars*) of  $\delta^{13}\text{C}$  in various diamond types compared with sedimentary carbon (data from Cartigny 2005) and typical  $\delta^{13}\text{C}$  for major carbon reservoirs (Schidlowski 1988, Cartigny 2005). The blue tick is the mode, and the red tick is the mean. The shaded vertical bands contain >90% of the samples of known provenance, and the dashed lines represent the averages. The range in diamonds is similar to that of sedimentary carbon, representing subduction into the mantle. Eclogitic diamonds associated with subducted oceanic crust show the expected signal from subducted carbon-rich material. Although previously unobserved, recent data from diamonds in the lower mantle (*purple lines*; Walter et al. 2011) suggest that this recycled material reaches significant depths via subduction. Abbreviation: UHP, ultrahigh pressure.

peridotite-hosted domains in the mantle. Elements including carbon that are strongly concentrated in subducted uppermost oceanic crust, oceanic sediments, and kimberlites relative to bulk mantle, however, are not significantly diluted by these processes and retain their isotopic compositions. Thus, kimberlites have great potential for hosting some geochemical signatures of early life.

Effects of photosynthesis are evident in post-Hadean kimberlites and their diamonds (**Figure 3**). The occurrence of negative  $\delta^{13}\text{C}$  in diamonds ultimately derived from subducted organic carbon is well known (Nisbet et al. 1994, Spetsius et al. 2009, Walter et al. 2011). Zartman & Richardson (2005) studied U/Th fractionation in kimberlites. As discussed above, oxidized environments mobilized uranium and not thorium (Rosing & Frei 2004). The inferred ratio of U/Th in the mantle source region of a kimberlite that erupted at  $\sim 2.7$  Gya had bulk Earth

value, indicating little selective surface mobilization of uranium at an early time of subduction. The U/Th ratio in younger kimberlites at present is twice the bulk Earth value, indicating increased uranium surface mobility at later subduction times.

Thallium isotope anomalies are a related example linked to redox conditions in the deep ocean, which went from anoxic to suboxic at  $\sim 1.85$  Gya (Slack et al. 2007, 2009; Slack & Cannon 2009). Thallium has two stable isotopes,  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$ . Circulating oxic cool seawater leaches thallium from shallow oceanic crust, preferentially mobilizing  $^{205}\text{Tl}$ . Manganese nodules accumulate this thallium on the seafloor, thereby sequestering  $^{205}\text{Tl}$ -rich material with Mn (Nielsen et al. 2006a). Nielsen et al. (2006b) detected the expected coupled variations of  $^{205}\text{Tl}/^{203}\text{Tl}$  with Mn in recent Hawaiian basalts.

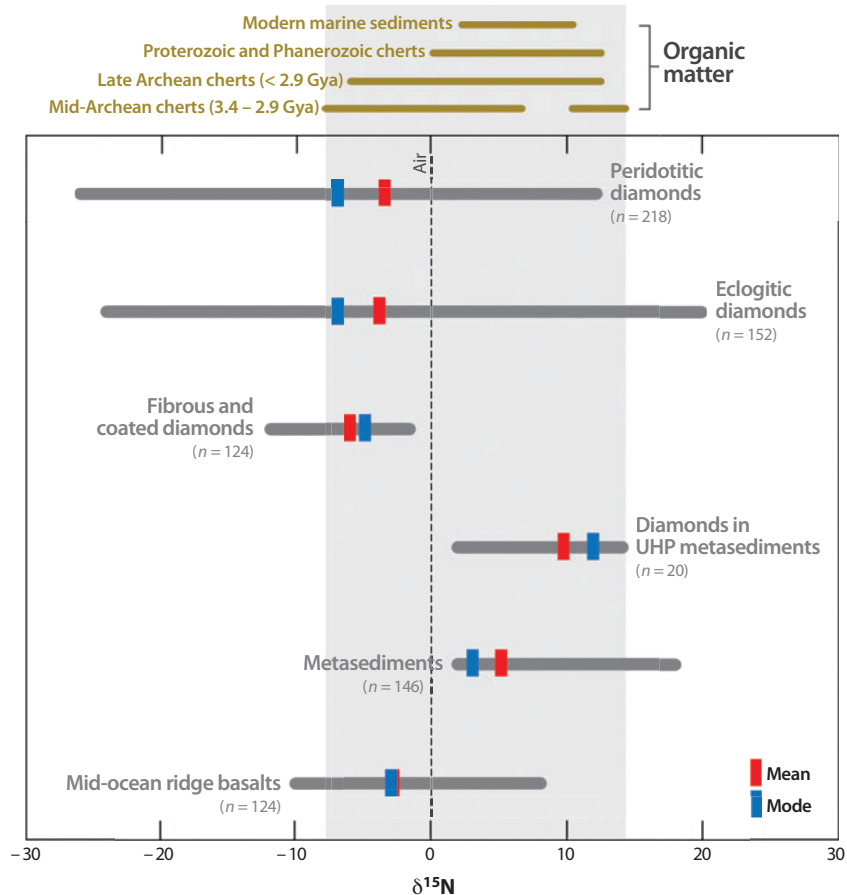
## Nitrogen and Ammonium

We review recent work on the mantle cycle of nitrogen that does not yet utilize Hadean samples. Nitrogen has two stable isotopes,  $^{14}\text{N}$  and  $^{15}\text{N}$ , that aid in tracing its biogeochemical cycles (**Figure 4**). By convention, the reference for  $\delta^{15}\text{N}$  is the present-day atmosphere.

Nitrogen, like carbon, is a biological element and prone to biologically mediated subduction in organic-rich sediments and altered crystalline rocks. The nitrogen in complex organic compounds decays to the ammonium ion ( $\text{NH}_4^+$ ) in black shale.  $\text{NH}_4^+$  substitutes for slightly smaller  $\text{K}^+$  in silicates in a process that occurs efficiently. For example,  $\text{NH}_4^+$  in clays is an exchangeable ion in agricultural soils (e.g., Liu et al. 2008) and low-temperature hydrothermal deposits (Šucha et al. 2007).  $\text{NH}_4^+$ -rich metamorphosed organic-rich sediments occur at the  $\sim 3.8$ -Ga-old Isua locality in Greenland (Papineau et al. 2005), indicating a minimum antiquity of the process.  $\text{NH}_4^+$ -bearing muscovite and potassium feldspar are stable in high-grade metamorphic rocks, such as in Greenland (Boyd 2001, Papineau et al. 2005) and under igneous conditions (e.g., Hall 1999). Hansma (2010) implicated muscovite as a nascent biotic venue because of its template properties, its occurrence in Hadean zircons (Hopkins et al. 2010), and its ability to sequester  $\text{NH}_4^+$  in its  $\text{K}^+$  site. We are not aware of any  $\delta^{15}\text{N}$  studies on such inclusions.  $\text{NH}_4^+$  stably enters silicates at high pressures, suggesting that the potential persistence of  $\text{NH}_4^+$ -rich domains in the mantle is likely (Watenphul et al. 2009, 2010).

Like carbon, subducted nitrogen is strongly concentrated in scattered lithologic domains and produces spatial heterogeneities during anatexis. Nitrogen behaves as a rare gas at shallow levels in basaltic magma chambers. Argon isotopes facilitate the recognition of the mantle source of  $\text{N}_2$ . Argon has three stable isotopes:  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$ .  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  are primordial rare gases that are strongly concentrated in the atmosphere.  $^{40}\text{Ar}$  is primarily a product of  $^{40}\text{K}$  decay and has a half-life of 1.248 Ga. This isotope has degassed into the air over geological time, but a significant fraction of the global inventory remains in the mantle. The concentration of  $\text{N}_2$  in lavas correlates with  $^{40}\text{Ar}$  but not  $^{36}\text{Ar}$  or  $^{38}\text{Ar}$ . This indicates that the magmatic nitrogen was associated with potassium in the mantle for a long geological time period and that the nitrogen resided as  $\text{NH}_4^+$  in K-bearing subducted silicate material (Marty & Dauphas 2003).

Nitrogen isotopic systematics of diamonds provides evidence for both Archean and later  $\text{NH}_4^+$  subduction. Nitrogen-rich diamonds (greater than  $\sim 100$  ppm) likely retain isotopic information on a subducted source that is not readily altered by ambient mantle nitrogen (**Figure 4**). Fractionated carbon isotopes in these diamonds support this inference. However,  $\delta^{15}\text{N}$  may have either sign in nitrogen-rich diamonds. This variation is most simply explained by the hypothesis that the sign of  $^{15}\text{N}$  fractionation in sediments from the atmosphere was negative in the Archean, when the atmosphere and ocean were anoxic, and positive after the Archean, when conditions were oxic (Marty & Dauphas 2003, 2004).



**Figure 4**

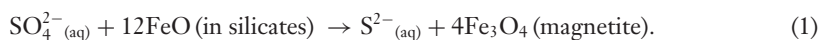
Ranges of  $\delta^{15}\text{N}$  in various diamond types, compared with sedimentary rocks, metasediments, and oceanic basalts. The shaded vertical region represents the range of  $\delta^{15}\text{N}$  in organic matter within unmetamorphosed sediments, which are divided by age at the top of the diagram. Only diamonds formed in ultrahigh-pressure crustal rocks (UHP metasediments) have high (>2,400-ppm) nitrogen contents (Cartigny 2005). Data from Marty & Dauphas (2003) and Cartigny (2005). Abbreviation: Gya, billion years ago.

The concentration of nitrogen in the mantle is still poorly constrained. Roughly, there is as much in the mantle as in the atmosphere. Goldblatt et al. (2009) gave 1.1 bar equivalent  $\text{N}_2$  as their minimum mantle reservoir, and  $\sim 0.4$  bar as their preferred crustal reservoir. They note, for comparison, that the atmospheric  $\text{N}_2$  per planetary mass in the Venus atmosphere is 3.4 times that of Earth. If this is the case, then Earth's present-day  $\text{N}_2$  atmosphere is a biologically modulated greenhouse gas, such as  $\text{CO}_2$ . It acts by increasing the total atmospheric pressure, thereby enhancing the effect of  $\text{CO}_2$  (Goldblatt et al. 2009, Li et al. 2009). Nitrogen from mantle-derived rocks will build up in the atmosphere if the climate is too cold for abundant photosynthetic life, causing global warming. Warm conditions facilitate photosynthesis,  $\text{NH}_4^+$  production, and  $\text{NH}_4^+$  subduction. The process is sluggish compared with the carbon cycle, but a more massive  $\text{N}_2$  atmosphere may explain, in part, why the Hadean and Archean Earth did not freeze over (cf. Rosing et al. 2010).

## Sulfur and Arc Volcanism: Less Brimstone in the Hadean

The global sulfur cycle differs from those of carbon and nitrogen in that the crust is only a minor global reservoir compared with the mantle. Holser et al. (1988) estimated  $350 \times 10^{18}$  mol for the crust and hydrosphere, with sedimentary sulfate, seawater sulfate, and sedimentary sulfide as the most important contributors. The sulfur concentration in the mantle is  $\sim 350$  ppm by mass (McDonough & Sun 1995), which implies  $\sim 43,750 \times 10^{18}$  mol, assuming that this concentration applies to the total mass of the mantle of  $\sim 4 \times 10^{24}$  kg. Hence, surface processes cannot significantly change the bulk mantle sulfur concentration.

However, surface processes do have large effects on the sulfur budget of high-temperature hydrothermal systems at ridge axes and of arc volcanism (Canfield et al. 2006). Sulfate is a significant ion in the modern ocean and ultimately a product of photosynthesis. Anoxygenic photosynthesis produced a finite marine sulfate concentration throughout the Archean. Sleep & Bird (2008) estimated that this concentration was  $\sim 10\%$  of the present marine level at the end of the Archean on the basis of global sulfur mass balances. Their reasoning involves reactions of sulfate with ferrous iron and calcium in the oceanic crust. In the Archean, sulfate that entered hot hydrothermal circulation quantitatively reacted with ferrous iron, with the net effect ignoring ion speciation

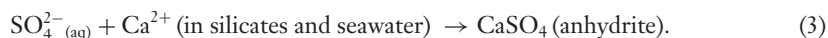


The dissolved sulfide further reacted with ferrous iron in silicates within the oceanic crust and in solution in seawater at the vents with the net effect



The flux of sulfur and oxygen in dissolved sulfate into the oceanic crust was proportional to the sulfate concentration in seawater. Hence, Reactions 1 and 2 acted as a buffer on this concentration. Other reactions of basalt with water also affect seawater pH, which has likely remained near its modern value of  $\sim 8$  since early Archean time (Friend et al. 2008).

Approximately 2.45 Gya, seawater sulfate reached  $\sim 10\%$  of its present level. The sulfate in excess of this concentration in hot hydrothermal systems reacted with calcium in the basalt to form anhydrite with the net reaction of



Anhydrite dissolved back into seawater once the crust cooled after moving away from the ridge axis. The flux of sulfate into oceanic crust in hydrothermal systems, and out of the crust away from the ridge axis, remained constant even as dissolved sulfate increased in seawater (Sleep & Bird 2008). Thus, the process acted as a sink with a finite flux rather than as a buffer that was controlled by seawater sulfate concentration, allowing dissolved sulfate in the ocean to increase from 10% to 100% of its present level.

The effect of low Hadean seawater sulfate concentration on the sulfide in vent fluids at ridge axes and on the sulfur in arc volcanoes was moderate (Hayes & Waldbauer 2006), so sulfide-rich regions remain reasonable prebiotic venues. At quasi-steady state, subduction returns the sulfur from oceanic crust and arc volcanoes to the mantle. The sulfur flux per area of oceanic crust does not change much with time, as the mantle concentration of sulfur does not change much. Sulfur in arc volcanics is derived partly from sulfide within the oceanic crust that formed from dissolved sulfate in seawater via Reactions 1 and 2, and hence is a product of photosynthesis. Intuitively, the concentration of sulfur in arc magmas is proportional to the quantity of subducted sulfur. The fluxes of sulfide at seafloor hydrothermal vents are derived from the sulfide dissolved from the oceanic crust and from sulfide derived from seawater sulfate that entered hydrothermal systems. At present, the two fluxes are comparable. In the early Archean, only the sulfide flux from the

oceanic crust was significant. The mass of sulfide per area of seafloor available to melt beneath island arcs was approximately half the present value. The sulfur concentration in arc magmas was thus approximately half its present value.

Despite its small fractional concentration in the crust, sulfur is a useful tracer of surface material. It has four stable isotopes: In terms of abundance,  $^{32}\text{S}$  is the major isotope,  $^{34}\text{S}$  is next, and  $^{33}\text{S}$  and  $^{36}\text{S}$  are quite rare. By convention, the standard reference ratio is a meteorite; hence the  $\delta$  values for the mantle are approximately 0;  $\delta^{34}\text{S}$  of arc volcanics is  $\sim 6\%$  (Alt 1995, Kump & Seyfried 2005). For example, a mixture of (a) 30% seawater sulfate from the slab (ultimately from photosynthesis) with  $\delta^{34}\text{S}$  of  $\sim 20\%$  and (b) magmatic sulfur with  $\delta^{34}\text{S}$  of  $\sim 0\%$  would yield this ratio (Sleep & Bird 2007). Deviations of arc-associated sulfide from  $0\%$  represent a durable record of an active sulfur cycle involving photosynthesis, as do sulfide inclusions in arc-related Hadean zircons (see Mojzsis 2007).

Use of all four sulfur isotopes provides evidence related to atmospheric oxygen concentrations. In most processes, sulfur isotopes fractionate according to their atomic masses (e.g., Farquhar et al. 2000, 2007; Pavlov & Kasting 2002; Kaufman et al. 2007; Papineau et al. 2007). Thus,  $\delta^{33}\text{S}$  is  $\sim 0.5\delta^{34}\text{S}$ , and  $\delta^{36}\text{S}$  is  $\sim 2\delta^{34}\text{S}$ . Mass-independent behavior of sulfur isotopes that occurs during photolysis in the atmosphere differs from the behavior indicated by these values. The abundant isotopes absorb ultraviolet radiation high in the atmosphere and shield sulfur species from the radiation in the lower atmosphere. The appropriate wavelength for the rare isotopes penetrates into the lower atmosphere, and photolysed sulfur species return to the ground or ocean in various places.

The Archean anoxic atmosphere enhanced this process to some extent, as there was more atmospheric sulfur to photolyse. Behavior of the photolysed sulfur species in the air, in the ocean, and on the ground was more important. Sulfur becomes sulfate under even weakly oxidizing conditions ( $\sim 2$  ppm in the air; Pavlov & Kasting 2002). Sulfate is highly soluble and well mixed within the much larger oceanic reservoir, recombining the material separated by photolysis. Significant mass-independent fractionation stopped at the end of the Archean ( $\sim 2.45$  Gya), indicating that at least trace oxygen was present in the air after that time. [See the review by Mojzsis (2007).]

The existence of mass-independent fractionation in a rock sample is thus both a  $>2.45$ -Gya time stamp and certification that the material was once at the surface (e.g., Farquhar et al. 2002). This signal is durable in that ordinary fractionation does not remove the effects of mass-independent fractionation. However, the massive sulfur reservoir in the mantle does dilute the effects of mass-independent fractionated domains.

The study of isotopic compositions of sulfide inclusions in diamonds links sulfur subduction to carbon and nitrogen subduction. Much care is needed in interpreting individual situations, however. Carbon and nitrogen bearing fluids move within the mantle. Hence, the diamond may be younger than its inclusions (Thomassot et al. 2009).

## Mantle Redox State

Photosynthesis conceivably affected the redox state of Earth's mantle over time. Mass-balance relationships indicate that the global effects are likely to be subtle. Only carbon with C(0) and C(IV) and iron with Fe(II) and Fe(III) have both significant concentrations and accessible multiple oxidation states in Earth's mantle. We express reservoir sizes in mol equivalent  $\text{O}_2$  to form the oxidized state from the reduced one—for example, the reaction  $4\text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ . We cite published estimates, as our arguments are not sensitive to the precise magnitude of the reservoirs. As a first-order approximation, the mantle and surface (crust plus ocean) reservoirs of  $\text{H}_2\text{O}$  and carbon are comparable.



The preferred mantle carbon reservoir of Hirschmann & Dasgupta (2009) contains  $9,750 \times 10^{18}$  mol of total carbon and  $O_2$  equivalent. Ferric iron provides  $15,000 \times 10^{18}$  mol equivalent  $O_2$  (Kuramoto & Matsui 1996). Water does not become  $H_2$  gas in the mantle unless a fluid is present. We give its abundance as 40% of the mass of the ocean ( $20,000 \times 10^{18}$  mol equivalent  $O_2$ ) (Kuramoto & Matsui 1996), as  $H_2$  escape to space is an ultimate source of available oxygen. The excess  $O_2$  in Earth's crust is only  $1,200 \times 10^{18}$  mol.

Resolving any small change of the bulk oxidation state of Earth's mantle is difficult because Fe(II) and Fe(III) reside as solid solutions in various minerals whose composition and stability are also sensitive functions of pressure and temperature. Geochemists have thus studied the partition of trace elements—including vanadium, scandium, and chromium—into magmas. Lee et al. (2005) stated that the mantle source regions of modern arc volcanoes have oxygen fugacities similar to those of mid-ocean ridge basalt, and Canil (2002) concluded that Archean source regions for arc magmas were similar to modern ones.

Still, subtle variations have been detected. Kelley & Cottrell (2009) showed that  $Fe(III)/[Fe(II)+Fe(III)]$  correlates with water content and increases from ridge axes to back-arc ridges to arcs. Dauphas et al. (2009) resolved small variations in  $Fe(III)/[Fe(II)+Fe(III)]$  over time and between source regions using iron-isotope ratios. Foley (2011) pointed out that redox reactions involving elemental carbon, methane,  $CO_2$ , and  $H_2O$  affect mantle melting, especially within domains derived from subducted crust, and that the extent and compositions of these domains likely varied over geological time.

Holland (2002, 2009) and Kump & Barley (2007) outlined a hypothesis that volcanic gasses control the net oxidation states of surface environments. Atmospheric oxygen built up when the gasses became more oxidized with time. We are skeptical for two reasons. First, the model of Holland (2009) explicitly involves subducted and recycled gasses, so cause and effect relations may be mingled. The source region of arc magmas became more oxidized with time as the concentration of sulfate entering axial hydrothermal systems increased. Second, the formation of volcanic gasses occurs at shallow levels at low pressure, and thermodynamically, the volcanic gasses are mobile components with low solubility in magma. The magma continues to produce additional  $SO_2$  and  $H_2$ , for example, as previous bubbles escape to the atmosphere. The oxygen to make  $SO_2$  from sulfide comes from Fe(III) in the magma;  $H_2$  escape adds oxygen from  $H_2O$  to the magma. The magma soon freezes, and the volcanic edifice eventually erodes and is mixed into the environment. Thus, degassing does not affect the net fluxes to surface environments over geological time.

With regard to kimberlites, carbonate-dominated domains behave differently from iron-dominated domains (Frost & McCammon 2008, Sleep 2009, Foley 2011). Solid solution in garnet stabilizes Fe(III) relative to Fe(II) at  $\sim 200$ -km depth, where kimberlites melt. Diamond is essentially a stoichiometric phase, so the fluid composition and the stability of other mineral phases do not depend on the amount of diamond present. Carbonates supply oxygen when their carbon forms graphite or diamond, so  $Fe(III)/[Fe(II)+Fe(III)]$  increases in a carbonate-rich domain until solid solution stabilizes the remaining Fe(II). We note that Martian magmatic source regions may be carbon dominated (Righter et al. 2008).

## Highly Reduced Mantle Minerals

The effect of photosynthesis needs appraisal even for reduced minerals in serpentinite. This rock type forms when olivine-rich rock reacts with water. The dominant minerals are serpentine [ideally  $(Mg,Fe)_3Si_2O_5(OH)_4$ ] and brucite [ideally  $(Mg,Fe)(OH)_2$ ]. Platinum-group native metals in serpentinite are potential prebiotic catalysts. They crystallize from magmas as trace phases along with chromite (e.g., Uysal 2008, Akbulut et al. 2010). Laurite ( $RuS_2$ ) is a trace magmatic

mineral commonly associated with chromite. Secondary platinum native metals form during the oxidation of laurite at shallow depths (Uysal et al. 2009), which ultimately involves photosynthesis. Moissanite (SiC)—along with iron-silicon metal compounds and native silicon—occurs as a rare component of mantle-derived rocks, including chromite-rich exhumed mantle and kimberlites (e.g., Trumbull et al. 2009). However, mantle SiC has strongly negative  $\delta^{13}\text{C}$ , indicating the possibility of subducted organic matter (Trumbull et al. 2009). Fang et al. (2009) described tungsten carbide (WC) and other strongly reduced minerals from chromite-rich mantle.

As an example of highly reduced mantle-derived material that does not require biologically reduced material to form, Lambert et al. (2010) suggested sodium silicate-rich fluid as an environment for abiotic formation of ribose. Carbonate and bicarbonate are soluble in these fluids, so there is no mass-balance carbon limitation.  $\text{SiO}_2$  is also soluble and, in this hypothesis, stabilizes ribose. Both anhydrous and hydrous sodium silicate minerals exist naturally in alkaline plutonic rocks (e.g., Pekov et al. 2007). Their formation requires  $\text{CO}_2$ -rich and alkali-rich magma but does not involve products of photosynthesis in any apparent way. Graphite forms during cooling and later reacts to form simple hydrocarbons (Ryabchikov & Kogarko 2009a,b). Thermodynamically, pyroxene crystallizing from sodium-rich magma has the Fe(III)-bearing component  $\text{NaFeSi}_2\text{O}_6$ , which stabilizes Fe(III) relative to Fe(II) in the magma. Removal of this oxygen into the solid reduces the remaining magma (Markl et al. 2010). Highly alkaline plutons thus are interesting, as they are rare potential indicators of prebiotic environments. There are several Archean examples, none of which has been analyzed for sodium silicates (Bizzarro et al. 2002, Rukhlov & Bell 2010).

In addition, extremely reducing conditions occur with the rapid formation and quenching of  $\text{H}_2$ -rich fluid. Fe(0)-Fe(II) acts as a buffer in sufficiently reduced iron-rich rocks. The strongest possible reductant in iron-poor hydrous environments is essentially water-saturated  $\text{H}_2$  gas at the confining pressure; materials such as potassium metal that rapidly reduce water are impossible. Dekov et al. (2009) reported native aluminum at the contact of a pegmatite intruded into serpentinite. Aluminum metal is too rare to be a serious contender for an abiotic catalyst, but it does illustrate the extreme reducing power of serpentinite.

Cosmic debris included much iron-nickel metal that produced fleeting but widespread reducing conditions (Kasting 1990). Most of the cosmic material arrived within large bodies that were transiently significant on Earth's surface (Zahnle et al. 2007, 2010) and that may have even produced a short-lived globally reducing atmosphere, as in the experiments of Miller & Urey (1959). However, Cleaves et al. (2008) and Johnson et al. (2008) showed that electrical sparks formed some amino acids at somewhat more oxidizing conditions, so such events do not seem necessary for life. The relative importance of cosmic processes was greater on the inactive surfaces of Mars and Ceres. As an example of a potential prebiotic catalyst, SiC is a strongly reduced component of meteorites (e.g., Trumbull et al. 2009). Meteorites also delivered reduced and reactive phosphorus minerals (Schwartz 2006, Pasek 2008). Lightning, including that within volcanic clouds, also produced reactive reduced phosphorus compounds (Schwartz 2006, Pasek & Block 2009). Zircon inclusion work (Harrison 2009, Hopkins et al. 2010) indicates that land environments and hence lightning targets existed in the Hadean; these findings are in line with this hypothesis.

## Marine Salinity

Subducted material retains geochemical information on specific environments and whether life inhabited these venues. Salinity is another important chemical signature because it provides information not only on surface conditions but also on the subduction of material into the deep mantle and its return to the surface. This observation justifies the assumption of whole-mantle convection in the mass-balance relationships.

Over geological time, NaCl accumulated as halite in restricted evaporite basins. The salt dissolved and returned to the ocean when these basins were exposed near the surface to rainwater and unsaturated marine water. This process required that there were enough continents to restrict marine circulation. Hence, it is expected that much of the surface inventory of NaCl resided in the ocean in the Hadean before large continents existed and that the Hadean salinity was twice that of the modern ocean (Morse & Mackenzie 1998, Knauth 2005). It is, in principle, possible to obtain paleosalinity by studying the substitution of  $\text{Cl}^-$  for  $(\text{OH})^-$  in hydrous minerals. Subduction zone fluids may well retain this signature.

A complicating factor is that NaCl-rich brines form by boiling in mid-ocean ridge magma-hydrothermal systems (e.g., Larson et al. 2009). Formation of NaCl-rich fluid beneath NaCl-poor subcritical fluid was pervasive as Earth cooled from its initial hot state. Earth's steam atmosphere contained most of its water and passed within a factor of 2 through the pressure conditions of modern ridge hydrothermal systems. NaCl-rich fluids formed in late basaltic magmas at 655–770°C (Larsen et al. 1992) represent an early condensate analog. NaCl-rich brine from boiling with hydrothermal systems at ridge axes represents fluid beneath a 400–500°C atmosphere.

The signature of NaCl-saturated young narrow oceans such as the Red Sea is more easily recognized. Diamonds from the Juina region of Brazil contain abundant halite inclusions, as well as sodium carbonates and sulfates (Kaminsky et al. 2009, Wirth et al. 2009), that would indicate a basaltic source altered beneath a hypersaline basin. These diamonds also contain high-pressure minerals, indicating that the source region traversed the lower mantle (Hayman et al. 2005, Kaminsky et al. 2009, Wirth et al. 2009). Negative  $\delta^{13}\text{C}$  in the Juina diamonds is compatible with subduction of organic matter (**Figure 3**; see also Kaminsky et al. 2009), although we note that the lower-mantle diamonds with organic carbon signatures studied by Walter et al. (2011) came from a different Juina kimberlite pipe and hence possibly a different mantle source region. The eruption ages of all of these Juina kimberlites are in the range of 92–95 million years, and the subduction age of the source region is unknown. In this regard, Harte & Richardson (2012) inferred that a mantle plume entrained material from a Mesozoic subducted slab into the source region for Juina, Brazil kimberlites. This process returned subducted material to the surface on a timescale between that of island arc volcanoes and that of general mantle circulation.

## DISCUSSION AND SYNTHESIS

Emergent life became more abundant only after photosynthetic oxidation of sulfide and ferrous iron evolved (Sleep & Bird 2008). Direct evidence of prephotosynthetic life is meager at best, with theoretical analysis of likely metabolic strategies guiding our inquiry (Canfield et al. 2006, Sleep & Bird 2007). However, there is possibility of a durable geologic record of prephotosynthetic life through the preservation of robust geochemical features. For example, methanogens, which were likely photosynthetic precursors (Sleep & Bird 2007), fractionate nickel isotopes (Cameron et al. 2009). One would also like to characterize climatic conditions in prebiotic times and during the emergence of life—for example, to distinguish oceanic crust formed beneath a hot  $\sim 200^\circ\text{C}$  massive  $\text{CO}_2$  greenhouse from that formed under a clement  $\sim 1$ -bar  $\text{CO}_2$  greenhouse. We do not have a good way to do this, and there is little agreement about the geologic and inferred climatic conditions of the early Earth (cf. Rosing et al. 2010, 2011; Dauphas & Kasting 2011; Goldblatt & Zahnle 2011; Reinhard & Planavsky 2011).

An indirect approach is warranted, as life has had a profound effect on surface geological processes, and even on modulated tectonics and the rise of continents (Rosing et al. 2006, Rollinson 2007). The net effect is Gaian (Lovelock 1979); that is, life has modified Earth to its net advantage.

Modification sometimes occurred globally, where the trait benefit for an individual microbe did not directly involve climate. Examples include ammonium subduction regulating atmospheric  $N_2$  and climate, as well as the Urey crustal  $CO_2$ -climate buffer. Ancient microbial mats and modern lichens on rocks benefited directly from their albedos' effects on their local environments, which led to global white and black Daisyworld effects (Wood et al. 2008). Global ecosystems have displaced one another several times over Earth history. Historically, Darwin [1958 (1872), chapter III] recognized that one ecosystem can displace another one, but he did not include ecosystem competition in his construct of the struggle for existence. It is not productive here to finely demarcate global ecosystem competition from Gaia.

The notable effects of photosynthetic life on Earth's crystalline crust and mantle give some expectation that evidence of its impact on crustal rocks during the Hadean can be found. Attractive venues include  $CO_2$ -rich kimberlites and carbonatites that are ultimately sourced by subducted uppermost oceanic crust, Hadean arc-related sulfides, and inclusions in Hadean zircons. Carbon isotopic fractionation is a strong biosignature, as are massive, reduced carbon-rich domains. As we show in this review, petrologists have picked the low-hanging fruit of Archean and younger biosignatures in the mantle, mainly through research initially directed at topics related to inorganic processes. Directed petrological effort is certainly warranted, as in the works of Foley (2011) and Walter et al. (2011). As a bonus, recognition of biological material in the mantle provides a tracer of deep Earth processes. For example, Walter et al. (2011) show that subducted material traversed the lower mantle.

One must not blindly extrapolate biologically rich Archean conditions back into the abiotic parts of the Hadean. We thus vetted putative prebiotic environments and catalytic minerals to see whether their existence is ultimately a product of photosynthesis. Fortunately, the effects of photosynthesis are minor in some likely venues, including hydrothermal vents from serpentinite (Amend & McCollom 2009, Lane et al. 2010, Russell et al. 2010) and weathering komatiites in the oceanic crust (Meunier et al. 2010).

There can be little doubt that the mantle preserves a rich record of life on Earth. We conclude that the well-defined post-Hadean biosignatures in the mantle give expectation of finding a Hadean record of life.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

## ACKNOWLEDGMENTS

We appreciate constructive comments from an anonymous reviewer. Ruth Blake, Wouter Bleeker, Vyllinniskii Cameron, Clark Friend, Suzanne Hangx, Tori Hoehler, Jim Kasting, Deborah Kelley, Nikola Koglin, Joseph Lambert, Derek Lovley, William Martin, Penny Morrill, Euan Nisbet, Minik Rosing, Elliott Sober, Boswell Wing, and Kevin Zahnle promptly answered questions. Stephen Mojzsis provided a thorough review of a draft. We acknowledge support from the National Science Foundation through grants NSF EAR-0406658 (to N.H.S.) and EAR-0408690 (to D.K.B.). This work was performed as part of our collaboration with the NASA Astrobiology Institute Virtual Planetary Laboratory Lead Team. Stanford University's Department of Geological and Environmental Sciences Endowment Fund provided support.

## LITERATURE CITED

- Abrams MD, Nowacki GJ. 2008. Native Americans as active and passive promoters of mast and fruit trees in the eastern USA. *Holocene* 18(7):1123–37
- Akbulut M, Pişkin Ö, Arai S, Özgeç İ, Minareci F. 2010. Base metal (BM) and platinum-group elements (PGE) mineralogy and geochemistry of the Elmaslar chromite deposit (Denizli, SW Turkey): implications for a local BM and PGE enrichment. *Ophioliti* 35(1):1–20
- Albarède F. 2009. Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* 461:1227–33
- Alt JC. 1995. Sulfur isotopic profile through the oceanic crust: sulfur mobility and seawater-crustal sulfur exchange during hydrothermal alteration. *Geology* 23:585–88
- Amend JP, McCollom TM. 2009. Energetics of biomolecule synthesis on early Earth. In *Chemical Evolution II: From the Origins of Life to Modern Society*, ed. L Zaikowski, JM Friedrich, SR Seidel, pp. 63–94. Washington, DC: Am. Chem. Soc.
- Bizzarro M, Simonetti A, Stevenson RK, David J. 2002. Hf isotope evidence for a hidden mantle reservoir. *Geology* 30(9):771–74
- Bowring SA, Williams IS. 1999. Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. *Contrib. Mineral. Petrol.* 134:3–16
- Boyd SR. 2001. Ammonium as a biomarker in Precambrian metasediments. *Precamb. Res.* 108:159–73
- Caldeira K. 1995. Long-term control of atmospheric carbon: low-temperature seafloor alteration or terrestrial silicate-rock weathering? *Am. J. Sci.* 295:1077–114
- Cameron V, Vance D, Archer C, House CH. 2009. A biomarker based on the stable isotopes of nickel. *Proc. Natl. Acad. Sci. USA* 106(27):10944–48
- Canfield DE, Rosing MT, Bjerrum C. 2006. Early anaerobic metabolisms. *Philos. Trans. R. Soc. B* 361:1819–36
- Canil D. 2002. Vanadium in peridotites, mantle redox and tectonic environments: Archean to present. *Earth Planet. Sci. Lett.* 195:75–90
- Cartigny P. 2005. Stable isotopes and the origin of diamond. *Elements* 1:79–84
- Catling DC, Zahnle KJ, McKay CP. 2001. Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Science* 293:839–43
- Cleaves HJ, Chalmers JH, Lazcano A, Miller SL, Bada JL. 2008. A reassessment of prebiotic organic synthesis in neutral planetary atmospheres. *Orig. Life Evol. Biosph.* 38:105–15
- Cvetkovic A, Menon AL, Thorgersen MP, Scott JW, Poole FL II, et al. 2010. Microbial metalloproteomes are largely uncharacterized. *Nature* 466:779–82
- Darwin C. 1958 (1872). *The Origin of Species*. New York: New Am. Libr. 479 pp. 6th ed.
- Dasgupta R, Hirschmann MM. 2007. Effect of variable carbonate concentration on the solidus of mantle peridotite. *Am. Mineral.* 92:370–79
- Dasgupta R, Hirschmann MM, McDonough WF, Spiegelman M, Withers AC. 2009. Trace element partitioning between garnet lherzolite and carbonatite at 6.6 and 8.6 GPa with applications to the geochemistry of the mantle and of mantle-derived melts. *Chem. Geol.* 262:57–77
- Dauphas N, Cates NL, Mojzsis SJ, Busigny V. 2007. Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada. *Earth Planet. Sci. Lett.* 254:358–76
- Dauphas N, Craddock PR, Asimow PD, Bennett VC, Nutman AP, Ohnenstetter D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth Planet. Sci. Lett.* 288:255–67
- Dauphas N, Kasting JF. 2011. Low  $p\text{CO}_2$  in the pore water, not in the Archean air. *Nature* 474, doi:10.1038/nature09960
- Dekov VM, Arnaudov V, Munnik F, Boycheva TB, Fiore S. 2009. Native aluminum: Does it exist? *Am. Mineral.* 94:1283–86
- Dixon J, Clague DA, Cousens B, Monsalve ML, Uhl J. 2008. Carbonatite and silicate melt metasomatism of the mantle surrounding the Hawaiian plume: evidence from volatiles, trace elements, and radiogenic isotopes in rejuvenated-stage lavas from Niihau, Hawaii. *Geochem. Geophys. Geosyst.* 9:Q09005
- Donnelly KE, Goldstein SL, Langmuir CH, Spiegelman M. 2004. Origin of enriched ocean ridge basalts and implications for mantle dynamics. *Earth Planet. Sci. Lett.* 226:347–66
- Fang Q, Bai W, Yang J, Xu X, Li G, et al. 2009. Qusongite (WC): a new mineral. *Am. Mineral.* 94:387–90



- Farquhar J, Bao HM, Thiemens M. 2000. Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289:756–58
- Farquhar J, Peters M, Johnston DT, Strauss H, Masterson A, et al. 2007. Isotopic evidence for Mesoarchean anoxia and changing atmospheric sulphur chemistry. *Nature* 449:706–9
- Farquhar J, Wing BA, McKeegan KD, Harris JW, Cartigny P, Thiemens MH. 2002. Mass-independent sulfur of inclusions in diamond and sulfur recycling on the early Earth. *Science* 298:2369–72
- Foley SF. 2011. A reappraisal of redox melting in the Earth's mantle as a function of tectonic setting and time. *J. Petrol.* 52:1363–91
- Francis D, Patterson M. 2009. Kimberlites and aillikites as probes of the continental lithospheric mantle. *Lithos* 109:72–80
- Friend CRL, Nutman AP, Bennett VC, Norman MD. 2008. Seawater-like trace element signatures (REE + Y) of Eoarchean chemical sedimentary rocks from southern West Greenland, and their corruption during high-grade metamorphism. *Contrib. Mineral. Petrol.* 155:229–46
- Frost DJ, McCammon CA. 2008. The redox state of Earth's mantle. *Annu. Rev. Earth Planet. Sci.* 36:389–420
- Gill JL, Williams JW, Jackson ST, Lininger KB, Robinson GS. 2009. Pleistocene megafaunal collapse, novel plant communities, and enhanced fire regimes in North America. *Science* 326:1100–3
- Goldblatt C, Claire MW, Lenton TM, Matthews AJ, Watson AJ, Zahnle KJ. 2009. Nitrogen-enhanced greenhouse warming on early Earth. *Nat. Geosci.* 2:891–96
- Goldblatt C, Zahnle K. 2011. Faint young Sun paradox remains. *Nature* 474, doi:10.1038/nature09961
- Hall A. 1999. Ammonium in granites and its petrogenetic significance. *Earth-Sci. Rev.* 45:145–65
- Hansma HG. 2010. Possible origin of life between mica sheets. *J. Theor. Biol.* 266:175–88
- Harrison TM. 2009. The Hadean crust: evidence from >4 Ga zircons. *Annu. Rev. Earth Planet. Sci.* 37:479–505
- Harte B, Richardson S. 2012. Mineral inclusions in diamonds track the evolution of a Mesozoic subducted slab beneath West Gondwanaland. *Gondwana Res.* 21(1):236–45
- Harvey LH. 1908a. Floral succession in the prairie-grass formation of southeastern South Dakota: serotinal and autumnal floral aspects. *Bot. Gaz.* 46(4):277–98
- Harvey LH. 1908b. Floral succession in the prairie-grass formation of southeastern South Dakota: the pre-vernial, vernal, and estival aspects. *Bot. Gaz.* 46(2):81–108
- Hayes JM, Waldbauer JR. 2006. The carbon cycle and associated redox processes through time. *Philos. Trans. R. Soc. B.* 361:931–50
- Hayman PC, Kopylova MG, Kaminsky FV. 2005. Lower mantle diamonds from Rio Soriso (Juina area, Mato Grosso, Brazil). *Contrib. Mineral. Petrol.* 149(4):430–45
- Hazen RM, Papineau D, Bleeker W, Downs RT, Ferry JM, et al. 2008. Mineral evolution. *Am. Mineral.* 93:1693–720
- Hirschmann MM, Dasgupta R. 2009. The H/C ratios of Earth's near surface and deep reservoirs, and the consequences for deep Earth volatile cycles. *Chem. Geol.* 262:4–16
- Holland HD. 2002. Volcanic gases, black smokers, and the great oxidation event. *Geochim. Cosmochim. Acta* 66:3811–26
- Holland HD. 2009. Why the atmosphere became oxygenated: a proposal. *Geochim. Cosmochim. Acta* 73:5241–55
- Holser WT, Schidlowski M, Mackenzie FT, Maynard JB. 1988. Geochemical cycles of carbon and sulfur. In *Chemical Cycles in the Evolution of the Earth*, ed. CB Gregor, RM Garrels, FT Mackenzie, JB Maynard, pp. 105–73. New York: Wiley
- Hopkins MD, Harrison TM, Manning CE. 2010. Constraints on Hadean geodynamics from mineral inclusions in >4 Ga zircons. *Earth Planet. Sci. Lett.* 298:367–76
- Iizuka T, Komiya T, Johnson SP, Kon Y, Maruyama S, Hirata T. 2009. Reworking of Hadean crust in the Acasta gneisses, northwestern Canada: evidence from in-situ Lu–Hf isotope analysis of zircon. *Chem. Geol.* 259:230–39
- Johnson AP, Cleaves HJ, Dworkin JP, Glavin DP, Lazcano A, Bada JL. 2008. The Miller volcanic spark discharge experiment. *Science* 322:404
- Kamber BS. 2010. Archean mafic-ultramafic volcanic landmasses and their effect on ocean-atmosphere chemistry. *Chem. Geol.* 274:19–28



- Kaminsky F, Wirth R, Matsyuk S, Schreiber A, Thomas R. 2009. Nyerereite and nahcolite inclusions in diamond: evidence for lower-mantle carbonatitic magmas. *Mineral. Mag.* 73(5):797–816
- Kasting JF. 1990. Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere. *Orig. Life Evol. Biosph.* 20:199–231
- Kaufman AJ, Johnston DT, Farquhar J, Masterson AL, Lyons TW, et al. 2007. Late Archean biospheric oxygenation and atmospheric evolution. *Science* 317:1900–3
- Kelley KA, Cottrell E. 2009. Water and the oxidation state of subduction zone magmas. *Science* 325(5940):605–7
- Knauth LP. 2005. Temperature and salinity history of the Precambrian ocean: implications for the course of microbial evolution. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 219:53–69
- Krauskopf KB, Bird DK. 1995. *Introduction to Geochemistry*. New York: McGraw-Hill. 647 pp. 3rd ed.
- Kulp TR, Hoefft SE, Asao M, Madigan MT, Hollibaugh JT, et al. 2008. Arsenic(III) fuels anoxygenic photosynthesis in hot spring biofilms from Mono Lake, California. *Science* 321(5891):967–70
- Kump LR, Barley ME. 2007. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* 448:1033–36
- Kump LR, Seyfried WE Jr. 2005. Hydrothermal Fe fluxes during the Precambrian: effect of low oceanic sulfate concentrations and low hydrostatic pressure on the composition of black smokers. *Earth Planet. Sci. Lett.* 235:654–62
- Kuramoto K, Matsui T. 1996. Partitioning of H and C between the mantle and core during the core formation in the Earth: its implications for the atmospheric evolution and redox state of early mantle. *J. Geophys. Res.* 101:14909–32
- Lambert JB, Gurusamy-Thangavelu SA, Ma K. 2010. The silicate-mediated formose reaction: bottom-up synthesis of sugar silicates. *Science* 327:984–86
- Lane N, Allen JF, Martin W. 2010. How did LUCA make a living? Chemiosmosis in the origin of life. *BioEssays* 32:271–80
- Larsen RB, Brooks CK, Bird DK. 1992. Methane-bearing, aqueous, saline solutions in the Skaergaard intrusion, east Greenland. *Contrib. Mineral. Petrol.* 112:428–37
- Larson BI, Lilley MD, Olson EJ. 2009. Parameters of subsurface brines and hydrothermal processes 12–15 months after the 1999 magmatic event at the Main Endeavor Field as inferred from in situ time series measurements of chloride and temperature. *J. Geophys. Res.* 114:B01207
- Lecuyer C, Ricard Y. 1999. Long-term fluxes and budget of ferric iron: implication for the redox states of the Earth's mantle and atmosphere. *Earth Planet. Sci. Lett.* 165:197–211
- Lee C-TA, Leeman WP, Canil D, Li Z-XA. 2005. Similar V/Sc systematics in MORB and arc basalts: implications for the oxygen fugacities of their mantle source regions. *J. Petrol.* 46:2313–36
- Li K-F, Pahlevan K, Kirschvink JL, Yung YL. 2009. Atmospheric pressure as a natural climate regulator for a terrestrial planet with a biosphere. *Proc. Natl. Acad. Sci. USA* 106(24):9576–79
- Liu Y-I, Zhang B, Li C-I, Hu F, Vlede B. 2008. Long-term fertilization influences on clay mineral composition and ammonium adsorption in a rice paddy soil. *Soil Sci. Soc. Am. J.* 72:1580–90
- Lovelock JE. 1979. *Gaia: A New Look at Life on Earth*. Oxford: Oxford Univ. Press. 157 pp.
- Markl G, Marks MAW, Frost BR. 2010. On the controls of oxygen fugacity in the generation and crystallization of peralkaline melts. *J. Petrol.* 51:1831–47
- Marty B, Dauphas N. 2003. The nitrogen record of crust-mantle interaction and mantle convection from Archean to Present. *Earth Planet. Sci. Lett.* 206:397–410
- Marty B, Dauphas N. 2004. “A large secular variation in the nitrogen isotopic composition of the atmosphere since the Archaean?": response to a comment on “The nitrogen record of crust-mantle interaction and mantle convection from Archaean to Present” by R. Kerrich and Y. Jia. *Earth Planet. Sci. Lett.* 225:441–50
- McDonough WF, Sun S-S. 1995. The composition of the Earth. *Chem. Geol.* 120:223–53
- Meunier A, Petit S, Cockell CS, El Albani A, Beaufort D. 2010. The Fe-rich clay microsystems in basalt-komatiite lavas: importance of Fe-smectites for pre-biotic molecule catalysis during the Hadean Eon. *Orig. Life Evol. Biosph.* 40:253–72
- Miller SL, Urey HC. 1959. Organic compound synthesis on the primitive Earth. *Science* 130:245–51
- Mojzsis SJ. 2007. Sulphur on the early Earth. *Dev. Precamb. Geol.* 15:923–70

- Mojzsis SJ, Arrhenius G, McKeegan KD, Harrison TM, Nutman AP, Friend CRL. 1996. Evidence for life on Earth before 3,800 million years ago. *Nature* 384:55–59
- Morse JW, Mackenzie FT. 1998. Hadean ocean carbonate geochemistry. *Aquat. Geochem.* 4:301–19
- Nakamura K, Kato Y. 2004. Carbonatization of oceanic crust by the seafloor hydrothermal activity and its significance as a CO<sub>2</sub> sink in the Early Archean. *Geochim. Cosmochim. Acta* 68:4595–618
- Nealson KH, Inagaki F, Takai K. 2005. Hydrogen-driven subsurface lithoautotrophic microbial ecosystems (SLiMEs): Do they exist and why should we care? *Trends Microbiol.* 13(9):405–10
- Nevle RJ, Bird DK, Ruddiman WF, Dull RA. 2011. Neotropical human-landscape interactions, fire, and atmospheric CO<sub>2</sub> during European conquest. *Holocene* 21(5):853–64
- Nielsen SG, Rehkamper M, Norman MD, Halliday AN, Harrison D. 2006a. Thallium isotopic evidence for ferromanganese sediments in the mantle source of Hawaiian basalts. *Nature* 439(7074):314–17
- Nielsen SG, Rehkamper M, Teagle DAH, Butterfield DA, Alt JC, Halliday AN. 2006b. Hydrothermal fluid fluxes calculated from the isotopic mass balance of thallium in the ocean crust. *Earth Planet. Sci. Lett.* 251:120–33
- Nisbet E, Zahnle K, Gerasimov MV, Helbert J, Jaumann R, et al. 2007. Creating habitable zones, at all scales, from planets to mud micro-habitats, on Earth and on Mars. *Space Sci. Rev.* 129:79–121
- Nisbet EG, Matthey DP, Lowry D. 1994. Can diamonds be dead bacteria? *Nature* 367:694
- Nutman AP, Friend CRL, Paxton S. 2009. Detrital zircon sedimentary provenance ages for the Eoarchean Isua supracrustal belt, southern West Greenland: juxtaposition of an imbricated ca. 3700 Ma juvenile arc against an older complex with 3920–3760 Ma components. *Precamb. Res.* 172:212–33
- Nutman AP, Mojzsis SJ, Friend CRL. 1997. Recognition of  $\geq 3850$  Ma water-lain sediments in West Greenland and their significance for the early Archean Earth. *Geochim. Cosmochim. Acta* 61:2475–84
- Papineau D. 2010. Mineral environments on the earliest Earth. *Elements* 6:25–30
- Papineau D, De Gregorio BT, Cody GD, Fries MD, Mojzsis SJ, et al. 2010. Ancient graphite in the Eoarchean quartz–pyroxene rocks from Akilia in southern West Greenland: I. Petrographic and spectroscopic characterization. *Geochim. Cosmochim. Acta* 74:5862–83
- Papineau D, Mojzsis SJ, Karhu JA, Marty B. 2005. Nitrogen isotopic composition of ammoniated phyllosilicates: case studies from Precambrian metamorphosed sedimentary rocks. *Chem. Geol.* 216:37–58
- Papineau D, Mojzsis SJ, Schmitt AK. 2007. Multiple sulfur isotopes from Paleoproterozoic Huronian interglacial sediments and the rise of atmospheric oxygen. *Earth Planet. Sci. Lett.* 255(1–2):188–212
- Pasek MA. 2008. Rethinking early earth phosphorus geochemistry. *Proc. Natl. Acad. Sci. USA* 105(3):853–58
- Pasek M, Block K. 2009. Lightning-induced reduction of phosphorus oxidation state. *Nat. Geosci.* 2:553–56
- Pavlov A, Kasting JF. 2002. Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* 2:27–41
- Pekov IV, Chukanov NV, Zadov AE, Zubkova NV, Pushcharovsky DYu. 2007. Chesnokovite, Na<sub>2</sub>[SiO<sub>2</sub>(OH)<sub>2</sub>] · 8H<sub>2</sub>O, the first natural sodium orthosilicate from the Lovozero alkaline pluton, Kola Peninsula: description and crystal structure of a new mineral species. *Geol. Ore Depos.* 49(8):727–38
- Plank T, Langmuir CH. 1992. Effects of the melting regime on the composition of the oceanic crust. *J. Geophys. Res.* 97(B13):19749–70
- Plank T, Langmuir CH. 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* 145:325–94
- Pons M-L, Quitté G, Fujii T, Rosing MT, Reynard B, et al. 2011. Early Archean serpentine mud volcanoes at Isua, Greenland, as a niche for early life. *Proc. Natl. Acad. Sci. USA* 108:17639–43
- Reinhard CT, Planavsky NJ. 2011. Mineralogical constraints on Precambrian pCO<sub>2</sub>. *Nature* 474, doi:10.1038/nature09959
- Righter K, Yang H, Costin G, Downs RT. 2008. Oxygen fugacity in the Martian mantle controlled by carbon: new constraints from the nakhlite MIL 03346. *Meteorit. Planet. Sci.* 43(10):1709–23
- Rollinson HR. 2007. *Early Earth Systems: A Geochemical Approach*. Malden, MA: Blackwell. 285 pp.
- Rosing MT. 1999. <sup>13</sup>C-depleted carbon microparticles in >3700-Ma sea-floor sedimentary rocks from west Greenland. *Science* 283:674–76
- Rosing MT, Bird DK, Sleep NH, Bjerrum CJ. 2010. No climate paradox under the faint early Sun. *Nature* 464:744–47

- Rosing MT, Bird DK, Sleep NH, Bjerrum CJ. 2011. Rosing, Bird, Sleep & Bjerrum reply. *Nature* 474, doi:10.1038/nature09960
- Rosing MT, Bird DK, Sleep NH, Glassley W, Albarede F. 2006. The rise of continents—an essay on the geologic consequences of photosynthesis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232:99–113
- Rosing MT, Frei R. 2004. U-rich Archean sea-floor sediments from Greenland—indications of >3700 Ma oxygenic photosynthesis. *Earth Planet. Sci. Lett.* 217:237–44
- Rukhlov AS, Bell K. 2010. Geochronology of carbonatites from the Canadian and Baltic Shields, and the Canadian Cordillera: clues to mantle evolution. *Mineral. Petrol.* 98:11–54
- Russell MJ, Hall AJ, Martin W. 2010. Serpentinization as a source of energy at the origin of life. *Geobiology* 8:355–71
- Ryabchikov ID, Kogarko LN. 2009a. Oxygen fugacity in the apatite-bearing intrusion of the Khibina complex. *Geochem. Int.* 47(12):1157–69
- Ryabchikov ID, Kogarko LN. 2009b. Redox potential of the Khibiny magmatic system and genesis of abiogenic hydrocarbons in alkaline plutons. *Geol. Ore Depos.* 51(6):425–40
- Sano Y, Williams SN. 1996. Fluxes of mantle and subducted carbon along convergent plate boundaries. *Geophys. Res. Lett.* 23:2749–52
- Saura E, Vergés J, Brown D, Lukito P, Soriano S, et al. 2008. Structural and tectonic evolution of western Cuba fold and thrust belt. *Tectonics* 27:TC4002
- Schidlowski M. 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* 333(6171):313–18
- Schwartz AW. 2006. Phosphorus in prebiotic chemistry. *Philos. Trans. R. Soc. B* 361:1743–49
- Shibuya T, Kitajima K, Komiya T, Terabayashi M, Maruyama S. 2007. Middle Archean ocean ridge hydrothermal metamorphism and alteration recorded in the Cleaverville area, Pilbara Craton, Western Australia. *J. Metamorph. Geol.* 25:751–67
- Shock EL. 2009. Minerals as energy sources for microorganisms. *Econ. Geol.* 104:1235–48
- Sibley DF, Vogel TA. 1976. Chemical mass balance of the Earth's crust: the calcium dilemma and the role of pelagic sediments. *Science* 192:551–53
- Slack JF, Cannon WF. 2009. Extraterrestrial demise of banded iron formations 1.85 billion years ago. *Geology* 11:1011–14
- Slack JF, Grenne T, Bekker A. 2009. Seafloor-hydrothermal Si-Fe-Mn exhalites in the Pecos greenstone belt, New Mexico, and the redox state of ca. 1720 Ma deep seawater. *Geosphere* 5(3):302–14
- Slack JF, Grenne T, Bekker A, Rouxel OJ, Lindberg PA. 2007. Suboxic deep seawater in the late Paleoproterozoic: evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. *Earth Planet. Sci. Lett.* 255:243–56
- Sleep NH. 2009. Stagnant lid convection and carbonate metasomatism of the deep continental lithosphere. *Geochem. Geophys. Geosyst.* 10:Q11010
- Sleep NH. 2010. The Hadean-Archean environment. *Cold Spring Harb. Perspect. Biol.* 2:a002527
- Sleep NH, Bird DK. 2007. Niches of the pre-photosynthetic biosphere and geologic preservation of Earth's earliest ecology. *Geobiology* 5:101–17
- Sleep NH, Bird DK. 2008. Evolutionary ecology during the rise of dioxygen in the Earth's atmosphere. *Philos. Trans. R. Soc. B* 363:2651–64
- Sleep NH, Bird DK, Pope EC. 2011. Serpentinite and the dawn of life. *Philos. Trans. R. Soc. B* 366:2857–69
- Sleep NH, Zahnle K. 2001. Carbon dioxide cycling and implications for climate on ancient Earth. *J. Geophys. Res.* 106:1373–99
- Sleep NH, Zahnle K, Neuhoff PS. 2001. Initiation of clement surface conditions on the early Earth. *Proc. Natl. Acad. Sci. USA* 98:3666–72
- Song S, Suc L, Niu Y, Lai Y, Zhang L. 2009. CH<sub>4</sub> inclusions in orogenic harzburgite: evidence for reduced slab fluids and implication for redox melting in mantle wedge. *Geochim. Cosmochim. Acta* 73:1737–54
- Spetsius ZV, Wiggers de Vries DF, Davies GR. 2009. Combined C isotope and geochemical evidence for a recycled origin for diamondiferous eclogite xenoliths from kimberlites of Yakutia. *Lithos* 112S:1032–42
- Stone D. 2010. Precambrian geology of the central Wabigoon subprovince area, northwestern Ontario. *Ont. Geol. Surv. Open File Rep.* 5422, Minist. North. Dev. Mines, Sudbury, Can.

- Šucha V, Uhlík P, Madejová J, Petit S, Kraus I, Puškelová L. 2007. Particle properties of hydrothermal ammonium-bearing illite-smectite. *Clays Clay Minerals* 55:36–44
- Sumner DY, Grotzinger JP. 1996. Were kinetics of Archean calcium carbonate precipitation related to oxygen concentration? *Geology* 24(2):119–22
- Tappe S, Foley SF, Kjarsgaard BA, Romer RL, Heaman LM, et al. 2008. Between carbonatite and lamproite—diamondiferous Torngat ultramafic lamprophyres formed by carbonate-fluxed melting of cratonic MARID-type metasomes. *Geochim. Cosmochim. Acta* 72:3258–86
- Tessalina SG, Bourdon B, Kranendonk M, Bircck JL, Philippot P. 2010. Influence of Hadean crust evident in basalts and cherts from the Pilbara Craton. *Nat. Geosci.* 3:214–17
- Thomassot E, Cartigny P, Harris JW, Lorand JP, Rollion-Bard C, Chaussidon M. 2009. Metasomatic diamond growth: a multi-isotope study ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ ) of sulphide inclusions and their host diamonds from Jwaneng (Botswana). *Earth Planet. Sci. Lett.* 282:79–90
- Thomazo C, Pinti DL, Busigny V, Ader M, Hashizume K, Philippot P. 2009. Biological activity and the Earth's surface evolution: insights from carbon, sulfur, nitrogen and iron stable isotopes in the rock record. *C. R. Palevol.* 8:665–78
- Trumbull RB, Yang J-S, Robinson PT, Di Pierro S, Vennemann T, Wiedenbeck M. 2009. The carbon isotope composition of natural SiC (moissanite) from the Earth's mantle: new discoveries from ophiolites. *Lithos* 113:612–20
- Turner G, Busfield A, Crowther S, Mojzsis SJ, Harrison TM, Gilmour J. 2007. Pu–Xe, U–Xe, U–Pb chronology and isotope systematics of ancient zircons from Western Australia. *Earth Planet. Sci. Lett.* 261:491–99
- Upadhyay D, Scherer EE, Mezger K. 2009.  $^{142}\text{Nd}$  evidence for an enriched Hadean reservoir in cratonic roots. *Nature* 459:1118–21
- Uysal İ. 2008. Platinum-group minerals (PGM) and other solid inclusions in the Elbistan-Kahramanmaraş mantle-hosted ophiolitic chromitites, southeastern Turkey: their petrogenetic significance. *Turkish J. Earth Sci.* 17:729–40
- Uysal İ, Zaccarani F, Sadiklar MB, Bernhardt H-J, Bigi S, Garuti G. 2009. Occurrence of rare Ru-Fe-Os-Ir-oxide and associated platinum-group minerals (PGM) in the chromitite of Muğla ophiolite, SW-Turkey. *N. Jb. Mineral. Abb.* 185(3):323–33
- Walter MJ, Kohn SC, Araujo D, Bulanova GP, Smith CB, et al. 2011. Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science* 334:54–57
- Walter RC, Merritts DJ. 2008. Natural streams and the legacy of water-powered mills. *Science* 319:299–304
- Watenphul A, Wunder B, Heinrich W. 2009. High-pressure ammonium-bearing silicates: implications for nitrogen and hydrogen storage in the Earth's mantle. *Am. Mineral.* 94:283–92
- Watenphul A, Wunder B, Wirth R, Heinrich W. 2010. Ammonium-bearing clinopyroxene: a potential nitrogen reservoir in the Earth's mantle. *Chem. Geol.* 270:240–48
- Wirth R, Kaminsky F, Matsyuk S, Schreiber A. 2009. Unusual micro- and nano-inclusions in diamonds from the Juina area, Brazil. *Earth Planet. Sci. Lett.* 286:292–303
- Witter JB, Kress VC, Newhall CG. 2005. Volcán Popocatepetl, Mexico. Petrology, magma mixing, and immediate sources of volatiles for the 1994–present eruption. *J. Petrol.* 46:2337–66
- Wood AJ, Ackland GJ, Dyke JG, Williams HTP, Lenton TM. 2008. Daisyworld: a review. *Rev. Geophys.* 46:RG1001
- Zahnle K, Arndt N, Cockell C, Halliday A, Nisbet E, et al. 2007. Emergence of a habitable planet. *Space Sci. Rev.* 129:35–78
- Zahnle K, Schaefer L, Fegley B. 2010. Earth's earliest atmospheres. *Cold Spring Harb. Perspect. Biol.* 2:a004895
- Zartman RE, Richardson SH. 2005. Evidence from kimberlitic zircon for a decreasing mantle Th/U since the Archean. *Chem. Geol.* 220:263–83



# Contents

Reminiscences From a Career in Geomicrobiology <i>Henry L. Ehrlich</i> .....	1
Mixing and Transport of Isotopic Heterogeneity in the Early Solar System <i>Alan P. Boss</i> .....	23
Tracing Crustal Fluids: Applications of Natural $^{129}\text{I}$ and $^{36}\text{Cl}$ <i>Udo Fehn</i> .....	45
SETI@home, BOINC, and Volunteer Distributed Computing <i>Eric J. Korpela</i> .....	69
End-Permian Mass Extinction in the Oceans: An Ancient Analog for the Twenty-First Century? <i>Jonathan L. Payne and Matthew E. Clapham</i> .....	89
Magma Oceans in the Inner Solar System <i>Linda T. Elkins-Tanton</i> .....	113
History of Seawater Carbonate Chemistry, Atmospheric $\text{CO}_2$ , and Ocean Acidification <i>Richard E. Zeebe</i> .....	141
Biomimetic Properties of Minerals and the Search for Life in the Martian Meteorite ALH84001 <i>Jan Martel, David Young, Hsin-Hsin Peng, Cheng-Yeu Wu, and John D. Young</i> ....	167
Archean Subduction: Fact or Fiction? <i>Jeroen van Hunen and Jean-François Moyen</i> .....	195
Molecular Paleohydrology: Interpreting the Hydrogen-Isotopic Composition of Lipid Biomarkers from Photosynthesizing Organisms <i>Dirk Sachse, Isabelle Billault, Gabriel J. Bowen, Yoshito Chikaraishi, Todd E. Dawson, Sarah J. Feakins, Katherine H. Freeman, Clayton R. Magill, Francesca A. McNerney, Marcel T.J. van der Meer, Pratigya Polissar, Richard J. Robins, Julian P. Sachs, Hanns-Ludwig Schmidt, Alex L. Sessions, James W.C. White, Jason B. West, and Ansgar Kabmen</i> .....	221

Building Terrestrial Planets <i>A. Morbidelli, J.I. Lunine, D.P. O'Brien, S.N. Raymond, and K.J. Walsh</i>	251
Paleontology of Earth's Mantle <i>Norman H. Sleep, Dennis K. Bird, and Emily Pope</i>	277
Molecular and Fossil Evidence on the Origin of Angiosperms <i>James A. Doyle</i>	301
Infrasound: Connecting the Solid Earth, Oceans, and Atmosphere <i>M.A.H. Hedlin, K. Walker, D.P. Drob, and C.D. de Groot-Hedlin</i>	327
Titan's Methane Weather <i>Henry G. Roe</i>	355
Extratropical Cooling, Interhemispheric Thermal Gradients, and Tropical Climate Change <i>John C.H. Chiang and Andrew R. Friedman</i>	383
The Role of H <sub>2</sub> O in Subduction Zone Magmatism <i>Timothy L. Grove, Christy B. Till, and Michael J. Krawczynski</i>	413
Satellite Geomagnetism <i>Nils Olsen and Claudia Stolle</i>	441
The Compositions of Kuiper Belt Objects <i>Michael E. Brown</i>	467
Tectonics of the New Guinea Region <i>Suzanne L. Baldwin, Paul G. Fitzgerald, and Laura E. Webb</i>	495
Processes on the Young Earth and the Habitats of Early Life <i>Nicholas T. Arndt and Euan G. Nisbet</i>	521
The Deep, Dark Energy Biosphere: Intraterrestrial Life on Earth <i>Katrina J. Edwards, Keir Becker, and Frederick Colwell</i>	551
Geophysics of Chemical Heterogeneity in the Mantle <i>Lars Stixrude and Carolina Lithgow-Bertelloni</i>	569
The Habitability of Our Earth and Other Earths: Astrophysical, Geochemical, Geophysical, and Biological Limits on Planet Habitability <i>Charles H. Lineweaver and Aditya Chopra</i>	597
The Future of Arctic Sea Ice <i>Wieslaw Maslowski, Jaclyn Clement Kinney, Matthew Higgins, and Andrew Roberts</i>	625
The Mississippi Delta Region: Past, Present, and Future <i>Michael D. Blum and Harry H. Roberts</i>	655



Climate Change Impacts on the Organic Carbon Cycle at the Land-Ocean Interface <i>Elizabeth A. Canuel, Sarah S. Cammer, Hadley A. McIntosh, and Christina R. Pondell</i> .....	685
--	-----

**Indexes**

Cumulative Index of Contributing Authors, Volumes 31–40 .....	713
Cumulative Index of Chapter Titles, Volumes 31–40 .....	717

**Errata**

An online log of corrections to *Annual Review of Earth and Planetary Sciences* articles may be found at <http://earth.annualreviews.org>



# ANNUAL REVIEWS

It's about time. Your time. It's time well spent.

## New From Annual Reviews:

### ***Annual Review of Statistics and Its Application***

Volume 1 • Online January 2014 • <http://statistics.annualreviews.org>

Editor: **Stephen E. Fienberg**, *Carnegie Mellon University*

Associate Editors: **Nancy Reid**, *University of Toronto*

**Stephen M. Stigler**, *University of Chicago*

The *Annual Review of Statistics and Its Application* aims to inform statisticians and quantitative methodologists, as well as all scientists and users of statistics about major methodological advances and the computational tools that allow for their implementation. It will include developments in the field of statistics, including theoretical statistical underpinnings of new methodology, as well as developments in specific application domains such as biostatistics and bioinformatics, economics, machine learning, psychology, sociology, and aspects of the physical sciences.

**Complimentary online access to the first volume will be available until January 2015.**

#### TABLE OF CONTENTS:

- *What Is Statistics?* Stephen E. Fienberg
- *A Systematic Statistical Approach to Evaluating Evidence from Observational Studies*, David Madigan, Paul E. Stang, Jesse A. Berlin, Martijn Schuemie, J. Marc Overhage, Marc A. Suchard, Bill Dumouchel, Abraham G. Hartzema, Patrick B. Ryan
- *The Role of Statistics in the Discovery of a Higgs Boson*, David A. van Dyk
- *Brain Imaging Analysis*, F. DuBois Bowman
- *Statistics and Climate*, Peter Guttorp
- *Climate Simulators and Climate Projections*, Jonathan Rougier, Michael Goldstein
- *Probabilistic Forecasting*, Tilmann Gneiting, Matthias Katzfuss
- *Bayesian Computational Tools*, Christian P. Robert
- *Bayesian Computation Via Markov Chain Monte Carlo*, Radu V. Craiu, Jeffrey S. Rosenthal
- *Build, Compute, Critique, Repeat: Data Analysis with Latent Variable Models*, David M. Blei
- *Structured Regularizers for High-Dimensional Problems: Statistical and Computational Issues*, Martin J. Wainwright
- *High-Dimensional Statistics with a View Toward Applications in Biology*, Peter Bühlmann, Markus Kalisch, Lukas Meier
- *Next-Generation Statistical Genetics: Modeling, Penalization, and Optimization in High-Dimensional Data*, Kenneth Lange, Jeanette C. Papp, Janet S. Sinsheimer, Eric M. Sobel
- *Breaking Bad: Two Decades of Life-Course Data Analysis in Criminology, Developmental Psychology, and Beyond*, Elena A. Erosheva, Ross L. Matsueda, Donatello Telesca
- *Event History Analysis*, Niels Keiding
- *Statistical Evaluation of Forensic DNA Profile Evidence*, Christopher D. Steele, David J. Balding
- *Using League Table Rankings in Public Policy Formation: Statistical Issues*, Harvey Goldstein
- *Statistical Ecology*, Ruth King
- *Estimating the Number of Species in Microbial Diversity Studies*, John Bunge, Amy Willis, Fiona Walsh
- *Dynamic Treatment Regimes*, Bibhas Chakraborty, Susan A. Murphy
- *Statistics and Related Topics in Single-Molecule Biophysics*, Hong Qian, S.C. Kou
- *Statistics and Quantitative Risk Management for Banking and Insurance*, Paul Embrechts, Marius Hofert

Access this and all other Annual Reviews journals via your institution at [www.annualreviews.org](http://www.annualreviews.org).

**ANNUAL REVIEWS | Connect With Our Experts**

Tel: 800.523.8635 (US/CAN) | Tel: 650.493.4400 | Fax: 650.424.0910 | Email: [service@annualreviews.org](mailto:service@annualreviews.org)

