Smaller, better, more: Five decades of advances in geochemistry

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ABSTRACT

Many of the discoveries made in geochemistry over the last 50 yr have been driven by technological advances that have allowed analysis of smaller samples, attainment of better instrumental precision and accuracy or computational capability, and automation that has provided many more data. These advances occurred during development of revolutionary concepts, such as plate tectonics, which has provided an overarching framework for interpreting many geochemical studies. Also, spacecraft exploration of other planetary bodies, including analyses of returned lunar samples and remote sensing of Mars, has added an additional dimension to geochemistry.

Determinations of elemental compositions of minerals and rocks, either through in situ analysis by various techniques (e.g., electron microprobe, secondary ion mass spectrometry [SIMS], synchrotron X-ray fluorescence [XRF], laser ablation) or bulk analysis (e.g., XRF, inductively coupled plasma–atomic emission spectrometry [ICP-AES], inductively coupled plasma–mass spectrometry [ICP-MS]), have become essential approaches to many geochemical studies at levels of sensitivity and spatial resolution undreamed of five decades ago. Although major-element distributions in igneous rocks have been understood at a basic level for some time, advances using major-element abundances to understand sedimentary provenance and processes have been especially noteworthy during the past half-century. The great diversity of trace elements in terms of geochemical behavior (e.g., lithophile, siderophile, etc.) has made them invaluable to many studies, providing unique constraints on redox conditions, mineral-melt and mineral-fluid reactions, and planetary differentiation.

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Significant advances in microanalytical techniques have markedly improved experimental determinations of trace-element partitioning among phases and in characterizing elemental distributions in rocks and minerals using two-dimensional (2-D) and three-dimensional (3-D) mapping. Rare earth elements, in particular, have proved to be invaluable tracers of magmatic, sedimentary, aqueous, redox, and cosmochronological processes, and siderophile trace elements form a basis for modeling many aspects of planetary accretion and early evolution. An anomalous amount of iridium at the Mesozoic-Cenozoic boundary has revolutionized our view of one of Earth’s most important biologic extinctions.

Isotopic variations, whether produced by stable or radiogenic isotopes, provide a third dimension to the Periodic Table of Elements, and tremendous advances in instrumentation since the early 1960s have greatly broadened this field of geochemistry. Early work outlined the stable H and O isotope fingerprints of natural waters and water-rock interactions, and stable C and S isotope studies defined the biological fractionations that occur by photosynthesis and microbial sulfate reduction, respectively, topics that have since been applied to problems relating to the evolution of life and Earth’s atmosphere. Recent work on stable O isotopes has documented the likelihood that liquid water existed >4 b.y. ago on Earth, which profoundly affects our view of Earth’s evolution. New work on “nontraditional” stable isotopes has investigated redox cycling over Earth’s history, as has study of non-mass-dependent stable isotope variations. New approaches using stable isotopes as paleothermometers include exploiting the unique energetics of bonds between rare stable isotopes. Early work on the radiogenic Rb-Sr and U-Th-Pb isotope systems documented the key distinctions between continental crust and mantle, setting the stage for later tracing of mass fluxes via plate tectonics, as well as documenting the great antiquity of continental crust formation and mantle differentiation on Earth. The Sm-Nd and Lu-Hf isotope systems provided a temporal context for earlier studies of rare earth element variations in nature, including new constraints on crustal growth rates and mechanisms extending back earlier than 4 Ga. The siderophile Re-Os isotope system has been used to study the accretion of planetary bodies, core-mantle interaction, and the nature of the ancient lithospheric mantle.

The branch of geochemistry that deals with fossilized organic molecules had its origins in elucidating the processes and pathways that led to petroleum formation. As awareness of the richness and diversity of organic compounds that can be preserved in sedimentary rocks grew, this gave way to the broader endeavor of molecular paleobiology. Despite great challenges in tying specific biomolecules to groups of organisms, or to metabolic processes, as well as issues of preservation mechanisms, molecular paleobiology remains a prime approach for studying the history of microorganisms, which have been the dominant life form for most of Earth’s history and yet are rarely preserved in the fossil record. Work on molecular biomarkers has produced numerous paleoenvironmental proxies for the chemistry and redox state (euxinia, anoxic, oxic) of the ancient oceans, as well as new paleoclimate records. The biochemical diversity of relatively simple life forms, including bacteria and archaea, has provided a wealth of lipid biomarkers that inform us about the evolution of metabolisms over Earth history, including oxygenic and anoxygenic photosynthesis, methanogenesis, and methanotrophy, and these records have been tied into stable isotope variations of many individual chemical elements (C, H, N, O, S, Fe, Mo, etc.), which provide a broad view of the biogeochemical evolution and biologically catalyzed redox cycling of Earth, and, potentially, other planetary bodies.

Although many geochemists focus exclusively on terrestrial problems, research over the past five decades has been intimately linked to the chemistry of other solar system bodies and the universe beyond. We routinely rely on meteorite falls, interplanetary dust particles, and Moon rocks for a baseline for comparison to Earth, which has been extensively differentiated and repeatedly resurfaced. Sophisticated
remote-sensing capabilities based on past and current spacecraft missions are enabling active study of other planetary bodies such as the Moon, Mercury, and Mars. Ideas about nucleosynthesis within stars are tested by reference to the measured isotopic compositions of tiny presolar grains extracted from chondrites. Short-lived radiouclides in meteorites provide a detailed record of the condensation, mixing, and differentiation history of the earliest solar system. Mass-independent oxygen isotope fractionation in extraterrestrial samples may identify photochemical processes in the early solar nebula. More broadly, the temperature stabilities of elements and minerals constrain the sequence of nebular condensation, which provides a first-order explanation for the bulk composition of the terrestrial planets relative to the planets of the outer solar system. Organic compounds from space inform us on the delivery of complex organic molecules to the early Earth, which likely influenced the earliest organic chemistry reactions, which in turn must have affected the origin and evolution of life. Chemical characterizations of samples of the Moon from the Apollo missions have provided the key data to recognize the Moon’s formation by impact of a Mars-size object with Earth and the likelihood that both bodies solidified from magma oceans.

The individual subfields in geochemistry are becoming increasingly integrated, where systems are now viewed in a more holistic fashion, such as multi-element or multi-isotopic studies of biogeochemical cycles. Such approaches seem likely to continue in the future, and they offer a comprehensive way to test multiple hypotheses and address geologic questions that continue to be important as we use geochemistry to better understand the geologic history of Earth and the solar system.

INTRODUCTION

Fifty years ago, in the early 1960s, modern geochemistry had begun to take shape, and from efforts during the first half of the twentieth century, many of its fundamental questions had come into focus. Even biogeochemistry, arguably the most modern branch of geochemistry, had been pioneered years earlier by Vernadsky and Baas Becking. The first journal specifically devoted to the field, *Geochimica et Cosmochimica Acta*, began publication in 1950. Two years later, the first English-language geochemistry text was published by Mason (1952), building on the pioneering efforts of his mentor Goldschmidt (whose classic tome was published posthumously two years later; Goldschmidt, 1954). The year 1952 also witnessed Nobel Prize–winning chemist Harold Urey publish his seminal book, *The Planets*, widely considered a pivotal event in what would become the field of cosmochemistry. In 1961, the American president John F. Kennedy laid down the challenge of sending humans to the Moon, and within a decade, intense competition for the opportunity to study returned lunar samples would result in major advances in geochemical techniques and thought.

On the other hand, the technical aspects of modern geochemistry were very much in their infancy 50 yr ago. Three examples illustrate this in the period leading up to our 50 yr review time frame. High-pressure, high-temperature experimental methods, pioneered at the Geophysical Laboratory by Norman Bowen during the first half of the twentieth century, were still only capable of exploring conditions relevant to the upper few kilometers of Earth by the early 1960s. In the early 1950s, distribution of the first international geochemical rock standards, G-1 and W-1, revealed a disturbing lack of agreement among the major geochemical laboratories of the world (e.g., Fairbairn et al., 1951), and analytical geochemists continued to struggle with data quality until the demanding standards of lunar sample analysis seeped through the broader geochemical community. Eventually, major strides were made as geochemical analyses moved away from techniques based on wet chemistry to those based on X-ray or mass spectra, allowing a marked increase in sample throughput. The use of chemical modeling in geochemistry has taken place almost entirely within the past 50 yr (Bethke, 2008). Garrels and Thompson (1962) first modeled the speciation of seawater, but the use of computers in geochemical modeling was not introduced until the work of Helgeson (1968).

Accordingly, our judgment is that developments in analytical, experimental, and modeling methods have largely facilitated the major advances of modern geochemistry during the last five decades. These developments have followed three simple but fundamental themes: smaller, better, and more. By smaller, we mean the capability to analyze increasingly smaller samples and thus to evaluate geochemical problems at increasingly finer scales. For example, analytical capabilities now often achieve subfemtogram (10−15 g) sensitivities, permitting study of vanishingly small samples, such as individual interstellar dust particles, or isotopic analysis of micron-sized regions of individual mineral grains. By better, we mean that modern geochemical methods permit ever-increasing precision, accuracy, and resolution, greater control on experimental conditions, and more stringent constraints on geochemical modeling. Thus, it is possible to measure many isotopic ratios with precisions approaching parts per million, and Moore’s law has witnessed >106 improvement in computing capabilities...
over the past 50 yr. By more, we mean that with modern methods, it is possible to study increasing numbers of samples and ever-widening geological conditions. For example, high-throughput mass spectrometers allow for construction of high-resolution paleoclimate proxy records; improvements in high-pressure experimental equipment (e.g., diamond anvils) allow for experiments to be carried out at conditions equivalent to the centers of terrestrial planets; improvements in chemical models permit evaluation of increasingly high ionic strength aqueous conditions. Importantly, these advances in instrumentation occurred during, and after, the emergence of plate tectonics, and in terms of providing a framework for terrestrial geochemical studies, plate tectonics permeated work in the field. Another conceptual advance in terrestrial geochemistry has been examination of Earth within a planetary perspective, with much insight coming from studies of meteorites and rocks from the Moon and Mars. Exploration of the solar system by spacecraft also occurred during this time, prodding the expansion of geochemical methods into remote sensing.

Our charge has been to summarize the remarkable progress that has been made in geochemistry during the last 50 yr in a journal-length chapter. We therefore begin with an apology to our colleagues for the large body of important work that must be omitted by the constraints imposed. Here, we are able to highlight only a small sample of the remarkable advances in geochemistry research in the last five decades. This contribution is intended to be useful for geochemists who desire a glimpse of progress in areas of research beyond their own, as well as generalists who are curious about what has been going on in those laboratories down the hall.

GEOCHEMISTRY OF THE ELEMENTS

Major- and trace-element compositions of rocks, minerals, and natural fluids have long been understood to be among the most fundamental data of geochemistry. Systematic evaluations of the abundances of the individual elements, and the basic laws governing their distributions in rocks and minerals were largely established by the 1960s, pioneered by the likes of Frank Clarke, Victor Goldschmidt, Louis Ahrens, and Ted Ringwood. Early analytical methods relied mainly on classical gravimetry and X-ray spectrographs to determine element compositions (Mason, 1992). During the 1950s, these laborious techniques began to give way to rapid and sensitive spectrophotometric methods, with the development and availability of instruments such as arc-source optical emission spectrographs and flame photometry, and chemical complexing agents (e.g., EDTA, ethylenediaminetetraet- tic acid) that could be used for colorimetry. Advances in bulk chemical analyses over the past 50 yr have witnessed astonishing developments of high-sensitivity instrumentation and methods (e.g., X-ray fluorescence, plasma-emission spectroscopy, neutron activation, chromatography, thermal ionization and plasma-source mass spectrometry), allowing for increasingly rapid and precise measurements of increasingly smaller samples (e.g., Gill, 1997; Sutton et al., 2006). A variety of microbeam methods further allows for determination of major- and trace-element (and isotope) compositions of very small volumes of minerals, and to spatially accumulate such data into two-dimensional (2-D) maps and three-dimensional (3-D) tomographic images of the compositions of rocks and minerals at micron to tens of micron scales of resolution.

Major-Element Geochemistry

Although early chemical analyses were time consuming, by the mid-twentieth century enough major-element data had been accumulated from igneous rocks to provide a basic appreciation of the ways in which fundamental magmatic processes (e.g., partial melting, equilibrium, and fractional crystallization) controlled observed variations (e.g., Harker and alkali-Fe-Mg [or AFM] diagrams). Because igneous and metamorphic processes are largely controlled by equilibrium, as shown, for example, by Norman Bowen’s studies of igneous systems, they are amenable to high-temperature, high-pressure experimental investigations, and experimental petrology has provided the fundamental background for interpreting chemical compositions. This work continues with the ability to carry out experiments at increasingly extreme conditions, for example, using diamond anvils that can attain pressures approaching the center of Earth (>300 GPa; Mao et al., 1990).

One area where fundamental advances in major-element geochemistry have been made over the past 50 yr is in microanalysis. The electron microprobe was developed during the first half of the twentieth century, but commercial probes only became available in the 1960s (Long, 1995). In order for these instruments to provide quantitative analyses of complex rock-forming minerals, improved understanding of the influences of atomic number, X-ray absorption and fluorescence (so-called ZAF corrections), and various matrix corrections (e.g., Bence and Albee, 1968; Reed, 1995) was required. Applications of rapid quantitative analysis of minerals are legion. Among the pioneering studies were evaluation of phase relations in high-pressure, high-temperature experiments, studies of diffusion from elemental profiles through minerals, quantitative study of coexisting mineral equilibria to constrain geothermometry, geobarometry, and oxygen fugacity (e.g., Andersen et al., 1993), and determination of mineral-melt partition coefficients in rocks and experiments allowing for quantitative geochemical modeling (see following).

In addition to the electron microprobe, other microbeam techniques have improved spatial resolution and sensitivity (i.e., detection limits) and allowed for elemental mapping (Jansen and Slaughter, 1982), including 3-D tomographic imaging (Jerram and Higgins, 2007). Examples include analytical electron microscopy, secondary ionization mass spectrometry, laser-ablation sources for emission and mass spectrometers, and synchrotron X-ray fluorescence microprobes. Figure 1 provides one example of modern geochemical mapping using a synchrotron X-ray fluorescence microprobe.
Five decades of advances in geochemistry

Sedimentary Geochemistry and the Chemical Index of Alteration (CIA) Concept

Unlike igneous systems, where major-element distributions have been studied in great detail for decades, interpretations of the elemental geochemistry of sedimentary systems until recently lagged far behind. The main reason for this is that siliciclastic sediments (sandstones, shales) are mostly physical mixtures and have been affected by multiple episodes of kinetically dominated water-rock interaction prior to, during, and after sedimentation. Accordingly, there was no simple measure, analogous to partition coefficients or Harker diagrams, that quantitatively linked bulk chemistry to process. Well into the 1970s, textbooks routinely tabulated chemical analyses of sedimentary rocks (e.g., Pettijohn, 1975) but provided little in the way of quantitative interpretation. Weathering processes were understood but focused primarily on gains/losses in soil profiles to evaluate weathering intensity as an index of paleoclimates. Experiments and field investigations made significant progress in evaluating the kinetics and time scales of weathering (Brantley and Lebedeva, 2011; White and Brantley, 1995). Garrels and Mackenzie (1971) first began to describe the relations between low-temperature aqueous geochemistry (e.g., mineral aqueous stability diagrams) and the bulk composition of sedimentary rocks.

Accordingly, a major advance in sedimentary geochemistry was development of the so-called chemical index of alteration (CIA) concepts during the 1980s and 1990s, in a series of papers by Wayne Nesbitt and coworkers (summarized in Nesbitt, 2003).

One especially influential diagram is the “feldspar ternary” diagram (in mole fraction), $\text{Al}_2\text{O}_3-(\text{CaO}^* + \text{Na}_2\text{O})-\text{K}_2\text{O}$, or A-CN-K (Fig. 2), where CaO* is CaO in silicate minerals only (i.e., corrected for carbonates and phosphates). The A-CN-K ternary diagram captures most of the major-element (and mineralogical) changes observed in weathering of igneous rocks (i.e., alteration of feldspar and glass to clay minerals). The CIA scale (CIA = $100 \times \text{Al}_2\text{O}_3/([\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}])$ is shown on the left side of Figure 2. This diagram also proves useful for interpreting the geochemistry of sedimentary rocks for several reasons: Minerals most relevant to sedimentary rocks plot at well-separated locations on the apices or along joins, and two-component mixing/unmixing relationships plot as straight lines and follow the lever rule. Accordingly, these relations have been used to quantify or constrain (1) the degree of weathering affecting sedimentary source regions, which typically has paleoclimatological implications; (2) mineral sorting and simple two-component mixing; (3) average provenance and mixing of provenance/mineral components; and (4) diagenesis. Variants on this diagram are the A-CNK-FM and A-CNKMF diagrams (F-FeO$_7$; M-MgO), which have less thermodynamic/kinetic foundation (Nesbitt and Young, 1984) but are especially useful in basaltic systems (Nesbitt and Wilson, 1992), and thus have been used in planetary applications (Hurowitz and McLennan, 2007; McSween and Keil, 2000).

Trace-Element Geochemistry

During the past five decades, some of the most significant advances in elemental chemistry have had to do with quantitative interpretations of trace-element distributions in rocks and minerals (as pioneered by Louis Ahrens, Paul Gast, Larry Haskin, Denis Shaw, and Ross Taylor), and these advances have naturally mirrored developments in analytical geochemistry.

Partition Coefficients

One such advance was the determination of partition coefficients (solid-liquid, solid-gas; expressed as K$_p$) from experiments and natural rock systems over a broad range of pressure-temperature-composition, beginning in earnest during the 1970s and 1980s. These data provided the foundation to the field of trace-element modeling of igneous processes (see reviews in Allègre and Minster [1978] and Green [1994]). Early studies were limited by the detection limits of the electron microprobe used to measure trace-element abundances in minerals and melts. Experiments were highly constrained by the necessary balancing act between having trace-element abundances high enough to be...
detected by the microprobe but not exceeding the Henry's law limit of remaining a trace element within the system (i.e., \( a_i = k x_i \), as \( x_i \Rightarrow 0 \) in some phase where \( i \) = element of interest, \( a \) = activity, \( x \) = molar concentration, and \( k \) = Henry's law constant). The development of highly sensitive modern microbeam techniques (e.g., ion microprobe, synchrotron X-ray fluorescence, laser-ablation mass spectrometry) now allows for precise determination of a wide range of partition coefficients, including those for highly incompatible elements (i.e., \( K_{\text{mineral/melt}} < 10^{-3} \)), under conditions that represent nature (e.g., Frei et al., 2009a).

**Rare Earth Elements**

The rare earth elements (REEs; La–Lu, Y) are the most studied and influential group of trace elements, and they have provided crucial evidence for a wide variety of geochemical and cosmochemical processes. In addition to elemental abundances, the REEs are used for several important radiogenic isotope systems (e.g., Sm-Nd, Lu-Hf), discussed later herein. REEs have been used to address problems ranging from constraining the earliest history of the solar nebula based on variations in condensation temperatures, coupled with measurements of their abundances in Ca-Al-rich inclusions and minerals in meteorites (Mason and Taylor, 1982), to tracing the movement of water masses through the oceans based on their short residence times (Piepgras and Wasserburg, 1980). The past five decades have also witnessed developments in the use of REEs as components for a variety of high-technology applications, such that these elements are now considered to be strategic metals, thus providing further impetus for future geochemical research (Haxel et al., 2005). Modern research on the REEs dates from the development of efficient separation methods and high-precision instrumental analytical techniques in the early 1960s that resolved, in the affirmative, the long-standing question of whether or not these elements could be fractionated during formation of Earth's crust (Haskin and Gehl, 1962).

By geochemical standards, REEs are an extremely coherent group in terms of size (ionic radius), charge, mineral cation site coordination, lithophile behavior, and aqueous complexing and speciation characteristics. From a planetary perspective, REEs

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1Scandium may also be considered a REE but typically is not included with the others in geochemical discussions due to its smaller size and differing partitioning behavior.
do not fractionate significantly during planetary formation from the solar nebula, and, accordingly, average chondritic meteorite abundances serve as a useful reference for examining planetary and geological processes. Under geological conditions, REEs are trivalent, except for the distinctive redox chemistries of europium (Eu$^{3+}$ or Eu$^{2+}$) and cerium (Ce$^{3+}$ or Ce$^{4+}$), which result in unique insights into magmatic and aqueous processes, respectively. Reduction of Eu (17% increase in ionic radius) occurs under highly reducing conditions, which, with rare exception, exist only within magmatic environments. On the other hand, oxidation of Ce (15% decrease in ionic radius) is common under surficial aqueous conditions, such as those encountered during weathering.

The REEs have proven particularly valuable for constraining magmatic processes because their mineral/melt partition coefficients, which (apart from Eu$^{2+}$) vary smoothly as a function of atomic number, vary over several orders of magnitude among the common rock-forming minerals (Fig. 3). For example, the ionic radius of Eu$^{2+}$ is virtually identical to that of Sr$^{2+}$ and readily substitutes for Ca$^{2+}$ in plagioclase. Accordingly, the presence of Eu anomalies in magmatic rocks commonly results from fractionation of plagioclase during partial melting or crystallization. Since plagioclase is stable only up to ~1 GPa pressure (~40 km depth on Earth), the presence of Eu enrichments or depletions in magmatic rocks generally indicates relatively shallow conditions. The ubiquitous presence of chondrite-normalized negative Eu anomalies in sedimentary rocks is thus interpreted to indicate that intracrustal igneous differentiation processes dominated formation of the upper continental crust (the source of sedimentary REEs). In another example, the presence of very steep REE patterns that are depleted in heavy REEs (high Gd/Yb) in magmatic rocks is taken to indicate fractionation of garnet, a mineral only stable at pressures higher than ~1 GPa in ultramafic systems and thus indicative of mantle origins. Accordingly, the origin of steep REE patterns in the ubiquitous Archean tonalite-trondhjemite-granodiorite suites has been central to development of models for the origin of Archean continental crust, and determination of whether or not the modern style of plate tectonics was operating at that time (Taylor and McLennan, 2009).

Although all REEs are cosmochemically refractory elements (50% $T_{\text{condensation}} > 1300$ K at 10 Pa), slight differences in their condensation temperatures lead to remarkably complex REE patterns in 4.567 Ga refractory Ca-Al–rich inclusions, the oldest material preserved in certain chondritic meteorites. In addition to unusual and highly variable overall shapes, the REE patterns of these objects also have both positive and negative anomalies involving the least refractory REEs (Ce, Eu, and Yb). These patterns thus provide persuasive evidence for very complex but relatively localized evaporation-condensation processes in the early solar nebula (Mason and Taylor, 1982).

The REEs have proven to be extremely useful tracers for understanding a wide range of aqueous processes (Byrne and Sholkovitz, 1996), primarily because they tend not to partition into the aqueous fluid ($D_{\text{fluid/solid}} << 1$) during fluid-rock interactions. Accordingly, REEs have been shown to be resistant to remobilization beyond the mineralogical scale during weathering, diagenesis, and metamorphism, except under conditions of very high fluid/rock ratios. REEs are particle-reactive and tend to be efficiently scavenged from seawater by sediment particles, resulting in very low residence times, ranging from ~50 yr (Ce) to ~2900 yr (Lu). In seawater, Ce is readily oxidized on Mn-oxide particle surfaces, and insoluble ceric oxides and hydroxides are then preferentially removed from seawater compared to the other trivalent REEs, resulting in extreme negative Ce anomalies. The stability constants for most REE complexes tend to increase with increasing atomic number, resulting in the light REEs (La–Sm) being preferentially scavenged over Gd–Lu. The overall effect of these characteristics is that REEs in natural fluids vary by many orders of magnitude in absolute abundances, with highly variable chondrite-normalized patterns, providing a very sensitive tracer.
Siderophile and Platinum Group Elements

A second group of trace elements that has proven especially useful for evaluating geochemical phenomena is the siderophile trace elements in general, including the refractory and highly siderophile platinum group elements (PGEs = Ru, Rh, Pd, Os, Ir, Pt). The major value of highly siderophile elements is their strong partitioning into metal phases during metal-silicate equilibrium (D_{metal liquid/silicate liquid} >> 10^3; Righter, 2003). Accordingly, their distributions provide insight into the nature of core-forming processes in planets and in the parent bodies of the various meteorite classes, and into the evolution of planetary mantles after extraction of cores.

One key discovery, based on PGE abundances, was that the mass extinction at the ca. 65 Ma Mesozoic-Cenozoic (Cretaceous-Paleogene; K-Pg) boundary was related to the impact of an asteroid, thus opening the door to an entirely new way to consider the relations between biologic evolution and geologic history. Alvarez et al. (1980) determined that clay-rich sediment deposited exactly at the K-Pg boundary was highly elevated in iridium, typically by ~20–200 times the levels in the enclosing sediments (Fig. 4). Since PGEs (including Ir) occur at very low levels in Earth’s mantle and crust due to sequestration into the metallic core during planetary differentiation, they argued that the likely source of globally distributed Ir was from impact of a large meteorite. Mass-balance calculations indicated the impactor, assuming a CI chondrite composition, would have been ~10 km in diameter. Much subsequent work, including the presence within the K-Pg sediment of additional PGE enrichments, as well as Re-Os isotope data, in addition to the presence of soot, shocked quartz, stishovite, and impact glass spherules, reinforced this model, and discovery of the buried ~200-km-diameter Chicxulub crater in Mexico with a 65.0 Ma age (e.g., Swisher et al., 1992), has confirmed that a major impact took place at that time.

Siderophile element distributions are also important in cosmochemistry (McSween and Huss, 2010). In addition to elemental abundances, siderophile elements possess important radiogenic isotope systems (e.g., Re-Os, Pt-Os, Hf-W) that provide details about planetary differentiation time scales (Kleine et al., 2009; Shirey and Walker, 1998). The family of siderophile elements encompasses a broad range of siderophile tendencies (as measured by metal-silicate partition coefficients under different pressure [P], temperature [T], and oxygen fugacity [f_O2] conditions), volatilities (condensation temperatures), and incompatibilities (mineral/silicate melt partition coefficients). Accordingly, they provide insights into core-mantle differentiation and silicate mantle melting in the terrestrial planets, Moon, and meteorite parent bodies (Righter, 2003; Righter and Drake, 1996; Walker, 2009).

ISOTOPE GEOCHEMISTRY

The field of isotope geochemistry offers the opportunity to look at the Periodic Table of Elements in a “third dimension,” where isotopic variations may result from stable isotope fractionation or radioactive decay. Isotope geochemistry provides an important means with which to trace mass fluxes among Earth’s reservoirs that are independent of concentration effects in the sense of activity coefficients and the thermodynamics of mixing. Historically, stable and radiogenic isotopes were studied by different laboratories, reflecting the distinct instrumentation required by various techniques, but such boundaries have now blurred. Our theme of “smaller, better, more” is embodied in the history of development of mass spectrometers. Modern mass spectrometers capable of high-precision isotopic measurements are based on the Nier (1940) geometry, and by the 1960s, the isotope ratio mass spectrometers (IRMS) available to the stable isotope community had a well-established dual-inlet system for comparing sample and standard gases, as well as simultaneous collection of two isotopes. Later, continuous-flow systems would come online (Hayes et al., 1990), and after that, online laser fluorination systems (Sharp, 1990). The thermal ionization mass spectrometers (TIMS) available to the radiogenic isotope community 50 yr ago, however, could not match the precision of dual-inlet, double-collector IRMS instruments. As electronics continued to improve, as well as the addition of multicollection, precisions attainable using TIMS instruments increased markedly in the 1980s (Thirlwall, 1991). Negative ion-capable TIMS later provided a breakthrough for the Re-Os isotope system (Creaser et al., 1991). A major innovation for both stable and radiogenic isotope geochemistry was development of a multicolonlector, magnetic-sector-based inductively coupled plasma–mass spectrometer (MC-ICP-MS) in the 1990s (Halliday et al., 1998). Finally, efforts have focused on in situ isotopic analysis at the micron scale from the 1990s to present. This includes secondary ion mass spectrometry (SIMS, or ion microprobe), where the current state-of-the-art, large-radius, multicollector instruments can determine δ^{13}C precisions, for example, of ±0.3‰ on ~10 µm spots (Valley and Kita, 2009). Laser-ablation (LA) coupled to MC-ICP-MS has also emerged as an important technique for in situ isotopic analysis, a technique widely applied, for example, to Hf isotope analysis (Griffin et al., 2000), and new research is currently investigating ultrafast (femtosecond; 10^{-15} s) lasers (Poitrasson et al., 2003).

Next, we touch on some of the major stable and radiogenic isotope systems used in geochemistry in the last five decades. Space limitations prevent us from covering some important isotopic systems, such as rare gas isotopes, which have seen important applications, for example, to mantle evolution using 3He/4He ratios (Kurz et al., 1982). Other important isotopic systems we have omitted include cosmogetic radionuclides, which, in solid Earth geochemistry, have provided unique constraints on sediment subduction using isotopes such as 10Be (Tera et al., 1986).

Stable Isotopes

Broadly, stable isotope variations reflect partitioning between phases that results from differences in zero-point energies for isotopically substituted species, although in detail, complexities exist that are mass-independent or reflect nonstochastic
distribution of rare isotopes. The basic thermodynamic framework for stable isotope geochemistry was laid out by Bigeleisen and Mayer (1947) and Urey (1947). Here, we focus on the main players that existed 50 yr ago, H, C, O, and S, followed by a discussion of newer stable isotope systems that have been developed since then.

**Hydrogen and Oxygen Isotopes**

The importance of water in the geologic cycle logically placed H and O isotopes as early targets in stable isotope geochemistry (Fig. 5). Significant accomplishments in the 1960s were numerous. The canonical relation between D/H and ¹⁸O/¹⁶O ratios of meteoric waters was determined (Craig, 1961), defining the meteoric water line, a relation that is a key factor to understanding the origin of fluids and fluid-rock interactions. The kinetic and equilibrium isotopic fractionations associated with meteoric waters, as well as temperature, latitude, and orographic effects, were established (Craig et al., 1963; Friedman et al., 1964), and especially large seasonal and temperature effects were documented in the δ¹⁸O values of precipitation in polar regions (Dansgaard et al., 1969; Epstein et al., 1963), setting the stage for use of oxygen isotopes from ice cores to infer paleoclimate. The δD-δ¹⁸O relations of hydrothermal waters that underwent fluid-rock interaction were recognized to be different from those produced by evaporation of meteoric waters (Craig, 1966). Initial efforts began to study the δ¹⁸O values of the ancient oceans when Perry (1967) suggested that the Precambrian oceans had much lower δ¹⁸O values than the modern ocean based on analysis of cherts. Muehlenbachs and Clayton (1976) proposed the important concept that the δ¹⁸O value of seawater was buffered near zero by extensive water-rock interactions at mid-ocean ridges (MORs), which would imply that the δ¹⁸O value of ancient seawater would be roughly invariant as long as plate tectonics operated. A landmark study of the Skaergaard intrusion combined detailed field studies with numerical modeling of convective heat transport to quantify water-rock interaction at a fossil hydrothermal system (Norton and Knight, 1977; Norton and Taylor, 1979). Studies of ophiolites (Gregory and Taylor, 1981) confirmed that extensive hydrothermal interaction at MORs has...
been responsible for fixing the d18O value of seawater. If the d18O value of seawater was relatively constant, the low-d18O values of Precambrian cherts could be interpreted to reflect very high ocean temperatures (Knauth and Epstein, 1976), although the possibility exists that very old samples have later exchanged with fluids that lowered their d18O values after deposition.

Oxygen isotope studies of igneous and metamorphic rocks in the 1970s and 1980s focused on (1) use of d18O values as a tracer of the sources of magmas, and (2) application of O isotope thermometry to metamorphism (Valley, 1986) and hydrothermal alteration (Gregory and Criss, 1986). The large decreases in d18O values that occur from meteoric hydrothermal alteration at elevated temperature (e.g., Criss and Taylor, 1983), or the large increases in d18O that occur during weathering (e.g., Savin and Epstein, 1970) produce a wide range in d18O values for upper-crustal rocks that may be incorporated into magmas. Elevated d18O values are characteristic of “S-type” granites, a term used for granites that contain a sedimentary component, and confirmed by O isotopes (O’Neil et al., 1977). In contrast, Friedman et al. (1974) discovered that magmas could attain low-d18O values through interaction with meteoric waters directly, or through assimilation of hydrothermally altered country rocks. Collectively, this discussion points to one of the most important contributions of stable O isotope geochemistry: A rock that has a d18O value that is distinct from that of the mantle probably contains O that was cycled near the surface of Earth in the presence of water (Taylor and Sheppard, 1986).

One of the most profound demonstrations of the use of O isotopes as a “water tracer” is found in the >4 Ga zircons from the Jack Hills, Western Australia, which have elevated d18O values, providing compelling evidence that liquid water existed on Earth over 4 b.y. ago (Cavosie et al., 2005; Mojzsis et al., 2001; Peck et al., 2001). This work, in fact, highlights the importance in isotope geochemistry of moving away from bulk sample analysis to in situ approaches (e.g., Valley and Kita, 2009). Without the ability to make precise, and accurate, O isotope analyses of micron-sized spots, the elevated d18O values found in the Jack Hills zircons would not have been discovered, and the concept of a “cool early Earth” (Valley et al., 2002) would not have arisen.

Carbon Isotopes

By 1960, it was already well established that photosynthetic fixation of CO2 into organic carbon produced a decrease in d13C values by −25‰ to −30‰ (Park and Epstein, 1960). In the following years, the first surveys of d13C values for marine carbonates and organic C confirmed that the overall isotopic fractionation between these C reservoirs can be found in natural samples, including those from Precambrian rocks (HoeFs and Schidlowski, 1967; Keith and Weber, 1964). As the database for C isotope compositions of carbonates greatly expanded in the following decade, it became clear that the vast majority of Ca-Mg marine carbonates had a restricted range in d13C values near zero for most of Earth history, which was interpreted to reflect a relatively constant balance between the organic and inorganic C reservoirs (Schidlowski et al., 1975). An important exception was Paleoproterozoic carbonates, which had unusually positive d13C values, first documented in the Lomagundi Group, Rhodesia (Schidlowski et al., 1975), and later shown to be global and correlated with a major rise in atmospheric oxygen, likely, at least in part, reflecting organic C burial (Karhu and Holland, 1996). In contrast to the generally zero d13C values for Ca-Mg carbonates, Fe-rich carbonates from Precambrian banded iron formations (BIFs) have significantly negative d13C values. Early workers suggested microbial oxidation of organic carbon as an explanation (Becker and Clayton, 1972), but later work favored vertical zonation in d13C values for dissolved inorganic carbon (DIC) in the oceans (Beukes et al., 1990; Winter and Knauth, 1992).

More recently, geochemical modeling and studies of shelf-to-basin transects suggest that vertical zonation in d13C values for DIC is unlikely, swinging the interpretation for negative d13C values back to microbial respiration (Beukes and Gutzmer, 2008; Fischer et al., 2009).

By the 1970s, there was already a substantial database for C isotope compositions of kerogen from Precambrian shales as old as 3.4 Ga, documenting that d13C values for organic carbon generally lay between −25‰ and −35‰ (Oehler et al., 1972). An important exception was discovery of highly negative d13C values for organic carbon in sedimentary rocks between ca. 2.8 and 2.6 Ga in age, down to −60‰. Such low values are accepted to reflect a role for involvement of methane, and Hayes (1983) speculated that aerobic methanotrophy might have been responsible. Follow-up work has confirmed these unusually low d13C values and documented correlations with sedimentary facies that suggest a transition from an anaerobic ecosystem to one supported by oxygenic photosynthesis at the end of the Archean (Eggenbrode and Freeman, 2006).

Looking at the oldest known sedimentary rocks, Schidlowski et al. (1979) noted that graphite in metasedimentary rocks from the Isua belt, SW Greenland, did not generally reach the low-d13C values that are characteristically thought to reflect photosynthetically fixed C, and this was interpreted to reflect the effects of metamorphism (Schidlowski, 1987). The importance of obtaining “primary” d13C values from C from Early Archean rocks, despite their commonly high grade of metamorphism, has generated numerous studies. Mojzsis et al. (1996) documented d13C values for graphite from Akilia Island, SW Greenland, obtained via in situ SIMS analysis, that were significantly lower than those measured in bulk samples, but this work has come under criticism on a number of fronts, including arguments (1) that the graphite is not photosynthetic in origin, but instead a breakdown product of Fe-bearing carbonates (van Zuilen et al., 2002), (2) that the sample analyzed was not a sedimentary rock but a metasomatic dike (Fedo and Whitehouse, 2002), and (3) that the graphite analyzed was not enclosed in apatite and therefore isolated from the effects of metamorphism (Lepland et al., 2005). The question of when the first C isotope compositions that suggest photosynthesis appeared on Earth remains an important one, although there is no consensus on the answer.
Recent work in C isotope geochemistry has expanded into in situ isotopic analyses, including studies of organic carbon and individual microfossils (House et al., 2000). Increasingly, it is recognized that the range in d\(^{13}\)C values for individual microfossils, or kerogen on submillimeter scales, is much larger than would be suggested by bulk C isotope analysis. Such an approach has affected the range in C isotope fractionations inferred between organic and inorganic C, which in turn may constrain atmospheric CO\(_2\) contents (Kauffman and Xiao, 2003), test the indigenous nature of molecular biomarkers (Rasmussen et al., 2008), or distinguish between eukaryotic and cyanobacterial photosynthesis (Williford et al., 2013).

**Sulfur Isotopes**

Early studies of S isotope variations in the laboratory and natural environments had documented a large fractionation in \(^{34}\)S/\(^{32}\)S ratios during microbial sulfate reduction that was dependent upon the rate of reduction and the abundance of sulfate, and similar ranges in isotopic compositions had been documented in modern marine sediments (Kaplan et al., 1963; Thode et al., 1961). In contrast to the strongly positive d\(^{34}\)S values measured for Phanerozoic sulfates, Perry et al. (1971) found that older than 3 Ga barites from South Africa had only slightly positive d\(^{34}\)S values, which they interpreted to reflect very low seawater sulfate contents, suggesting very low atmospheric O\(_2\) contents. Detailed experimental work on microbial reduction and S disproportionation in the 1990s demonstrated that extremely large \(^{34}\)S/\(^{32}\)S fractionations could be produced during microbial S cycling that involved S species of intermediate oxidation state such as sulfite and thiosulfate (Canfield and Thamdrup, 1994; Canfield and Teske, 1996). This in turn suggested that the exceptionally low d\(^{34}\)S values in sedimentary sulfides of younger than 1 Ga age reflected an increase in the oxidative component of the S cycle, which in turn provided strong evidence for a major rise in atmospheric O\(_2\) contents in the Neoproterozoic. The decrease in d\(^{34}\)S values of sulfides in the Neoproterozoic, relative to earlier time periods, was accompanied by an increase in the estimated d\(^{34}\)S values for seawater sulfate (Canfield, 2001).

Burdett et al. (1989) proposed that the isotopic compositions of seawater sulfate may be determined through analysis of carbonate-associated sulfate (CAS), an approach that greatly extends the lithologies that may be used to infer ancient seawater S. The CAS proxy proved particularly valuable for the ancient rock record, where the d\(^{34}\)S values of ancient seawater sulfate had been previously inferred indirectly based on the maximum values obtained in a suite of sedimentary sulfides. Application of the CAS proxy to the Proterozoic has confirmed expectations that seawater sulfate contents were very low in the Paleoproterozoic, before or immediately after the Great Oxidation Event (GOE), but rose substantially in the Neoproterozoic at the time of the second increase in atmospheric oxygen (Kah et al., 2004).

The last decade has seen a rapid increase in in-situ S isotope studies, primarily focused on pyrite. These efforts have shown that detrital, authigenic, and hydrothermal components may be recognized in the same single pyrite grain (Williford et al., 2011). Work on ca. 3.4 Ga rocks from the Pilbara craton, Australia, has documented significant S isotope variations on the micron scale, which have been generally interpreted to reflect biological cycling of S, including S\(^{8}\) disproportionation and sulfide reduction (Phillippot et al., 2007; Wacey et al., 2011). A very large range in d\(^{34}\)S values, >35\%, was observed in pillow lava textures in the Barberton greenstone belt, which were interpreted to reflect microbial microboring, and which McLoughlin et al. (2012) suggested provides evidence for a Paleoarchean subsea-floor biosphere.

**Mass-Independent Stable Isotopes**

Most stable isotope variations in terrestrial systems fractionate in a mass-dependent manner. Mass-independent fractionations (MIF) for O isotopes (and others) are commonly observed in extraterrestrial samples (Birck, 2004), and will be discussed later in this review. Sulfur MIF (commonly termed “S-MIF”) has been studied extensively in ancient sedimentary rocks as a tracer of past atmospheric O\(_2\) contents. The most common mechanism called upon to produce S-MIF is photolysis reactions involving SO\(_2\) and H\(_2\)S in the upper atmosphere, based on ultraviolet (UV) radiation experiments (Farquhar et al., 2001, 2000b). Because ozone is a strong absorbent of UV in the atmosphere, its presence would greatly decrease S-MIF in aerosols, which suggests that the S-MIF recorded in Archean and Paleoproterozoic rocks indicates very low atmospheric O\(_2\) contents (Farquhar et al., 2000a). Photochemical modeling suggests that transport of S-MIF to the sedimentary cycle requires ambient atmospheric oxygen contents less than 10\(^{-5}\) of present day (Pavlov and Kasting, 2002). The specific mechanisms and pathways responsible for creating S-MIF in the ancient rock record, however, remain unclear, where initial UV experiments may not have adequately modeled the full spectrum of UV radiation, and the roles of other gases, including methane and inert gases, are issues that have been raised (e.g., Domagal-Goldman et al., 2008; Lyons, 2009; Masterson et al., 2011; Zahnle et al., 2006). Further complexity arises from the finding that thermochemical sulfate reduction by organics can produce mild S-MIF (Watanabe et al., 2009). Nevertheless, most workers accept S-MIF in Archean and Paleoproterozoic sedimentary sulfides as indicating essentially anoxic conditions in Earth’s atmosphere at this time, although research continues on the ancient rock record, as well as the mechanisms to produce MIF.

**Nontraditional Stable Isotopes**

Nearly three quarters of the elements on the Periodic Table of Elements have two or more stable isotopes, but beyond the stable isotope systems discussed here, and a few others, most elements have remained relatively unexplored due to analytical barriers or the opinion that the range of isotopic variations in nature is too small to be worth the trouble. Vanguard efforts in the “nontraditional” stable isotopes include early studies of Li (Chan, 1987), Si (Douthitt, 1982), and Ca (Russell et al., 1978)
isotopes. The largest isotopic variations of the “nontraditional” stable isotopes are observed for Li, where the range in $^{7}$Li/$^{6}$Li in nature exceeds 75‰ (Tomasasc, 2004). Smaller variations are found for intermediate-mass elements, where, for example, $^{32}$Mg/$^{24}$Mg, $^{64}$Ca/$^{40}$Ca, $^{39}$K/$^{40}$K, $^{54}$Ti/$^{44}$Ti, $^{56}$Fe/$^{54}$Fe, $^{60}$Cu/$^{62}$Cu, $^{75}$Se/$^{77}$Se, and $^{95}$Mo/$^{97}$Mo ratios vary by $\Delta$2‰–10‰ in natural samples (e.g., Albarède, 2004; Anbar, 2004; Beard and Johnson, 2004a; DePaolo, 2004; Johnson and Bullen, 2004; Young and Galy, 2004). Results from additional stable isotope systems are being regularly reported at meetings and in publications, extending all the way up to mass U (e.g., Weyer et al., 2008). The field is changing so rapidly that the first review of the subject in 2004 is now significantly out of date (Johnson et al., 2004).

One of the most intensively studied “nontraditional” stable isotope systems has been Fe. The large bonding changes that occur between Fe$^{3+}$ and Fe$^{2+}$ species in solutions and minerals were recognized early as the major driving force for producing Fe isotope fractionations (Beard et al., 1999; Bullen et al., 2001; Johnson et al., 2002; Polyakov and Mineev, 2000). The vast majority of Fe in the crust has a $^{56}$Fe value near zero, including low-C, low-S sedimentary rocks (Beard et al., 2003a, 2003b) and most igneous rocks, although there are small variations in high-temperature rocks (Beard and Johnson, 2004b). The largest range in $\delta^{56}$Fe values, however, is restricted to organic-rich shales and BIFs, which vary from $\delta$−4‰ to +2‰ (Johnson et al., 2008a; Rouxel et al., 2005; Yamaguchi et al., 2005). The origin of such large variations is debated, where some workers argue that they reflect variable extents of oxidation of aqueous Fe$^{2+}$ (Anbar and Rouxel, 2007), and others interpret such variations, particularly in Fe-rich rocks, to reflect microbial Fe$^{3+}$ reduction (Johnson et al., 2008b). Recently, multiple stable isotope systems have been used to study redox-driven geochemical cycling, greatly expanding the utility of stable Fe isotopes, including Fe and S isotopes (Archer and Vance, 2006), Cr isotopes and Fe redox changes (Frei et al., 2009b), Fe and C isotopes, including carbonate C (Heimann et al., 2010) and organic C (Czaja et al., 2010), and Fe and Mo isotopes (Czaja et al., 2012). In summary, the field of nontraditional stable isotopes is growing rapidly, although progress is currently hampered by the relative paucity of stable isotope fractionation factors as compared to other stable isotope systems that have been studied for several decades.

### Clumped Stable Isotopes

Stable isotope compositions generally consider substitution of a single minor isotope, such as $^{13}$C$^{18}$O$^{16}$O or $^{12}$C$^{18}$O$^{16}$O in carbon dioxide because multiply substituted minor isotopes, such as $^{13}$C$^{18}$O$^{16}$O, are very low in abundance in nature. Recently, however, the unique aspects of multiply substituted minor isotopes have been exploited (Wang et al., 2004). Now termed “clumped-isotope” geochemistry, to describe, for example, the enhanced stability of $^{13}$C$^{18}$O bonds in CO$_{2}$ and carbonates relative to a random or stochastic distribution of minor isotopes, this field of stable isotope geochemistry promises great breakthroughs in paleoclimate studies, which require accurate determination of paleotemperatures, as well as the study of atmospheric gases (Eiler, 2007). For CO$_{2}$ and carbonate, the measured enrichment in $^{13}$C$^{18}$O bonds relative to that expected for a random distribution of $^{13}$C$^{18}$O bonds is defined as $\Delta_{\text{cl}}$, reflecting nominal mass 47 for $^{13}$C$^{18}$O$^{16}$O, and this has been shown to be an inverse function of temperature (Ghosh et al., 2006). Because the enhanced stability, or “clumping,” of $^{13}$C$^{18}$O bonds, under equilibrium conditions, reflects internal, homogeneous equilibrium that is independent of the bulk d$^{13}$C or d$^{18}$O values, $\Delta_{\text{cl}}$ provides an “internal” thermometer that does not require knowledge of the isotopic composition of the fluid from which the carbonate precipitated. This critical aspect of “clumped-isotope” geochemistry obviates the need to know, or assume, the d$^{18}$O or d$^{13}$C value of ancient seawater when extracting paleotemperatures from marine carbonates. Clumped stable isotopes therefore hold great promise for resolving debates such as the temperatures of the Archean oceans (Kasting et al., 2006; Knauth, 2005). An important component to using clumped isotope thermometry is the preliminary observation that the “vital” effects that are known to fractionate $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O ratios during biologically catalyzed carbonate formation in marine environments do not apparently affect $\Delta_{\text{cl}}$ values (Thiagarajan et al., 2011; Tripati et al., 2010). There seems little doubt that as the very demanding analytical issues of clumped-isotope geochemistry are tackled by more laboratories, and refined with improvements and new directions in instrumentation and experimental studies, this area of stable isotope geochemistry will expand.

### Radiogenic Isotopes

Radiogenic isotopes may be used for geochronologic information, or as a genetic tracer. Here, we will generally cover the latter, as the subject of geochronology is covered in another chapter in this series, but it should be recognized that radiogenic isotope systems often provide both types of information. The following discussion is grouped by isotope system, as is traditionally done, but we note that modern radiogenic isotope studies commonly combine multiple isotopic systems, blurring such grouping of subjects.

#### Rb-Sr

The isotope $^{87}$Rb decays to $^{86}$Sr with a half-life ($t_{1/2}$) of 49 b.y. Work in the 1960s established that Precambrian continental crust had significantly higher $^{87}$Sr/$^{86}$Sr ratios than mantle-derived rocks, reflecting the higher time-integrated $^{87}$Rb/$^{86}$Sr ratios of continental crust (Faure and Hurley, 1963). Early studies of the mantle documented Sr isotope heterogeneity across tholeiitic and alkaline basalts, but they documented a generally nonradiogenic (low $^{87}$Sr/$^{86}$Sr) isotopic composition that was similar to aachondrite meteorites (Engel et al., 1965). In contrast, the first studies of granitic batholiths showed intermediate $^{87}$Sr/$^{86}$Sr ratios, suggesting they were composed of mixtures of mantle and crustal material (Hurley et al., 1965). A landmark paper by Kistler and Peterman (1973) on the Sierra Nevada batholith documented across-arc
variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that correlated with outcrop patterns of Precambrian rocks. Following contouring of the data, they proposed that a line of initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.706$ marked the boundary of the continental crust. The 1980s saw an increased focus on interaction between arc magmas and continental crust, including many studies that combined O and Sr isotopes. Taylor (1980) and DePaolo (1981b) advanced the idea of coupled assimilation and fractional crystallization, drawing upon heat balance arguments put forth decades earlier by Norman Bowen. Numerous studies on the covariation of O and Sr isotopes in granitic batholiths provided constraints on the crustal lithologies that were blended in arc magmas, as well as insights into deep crustal architecture (e.g., Fleck and Criss, 1985; Solomon and Taylor, 1989).

There has long been an interest in the Sr isotope composition of seawater, and Faure et al. (1965) made one of the first measurements of modern seawater, found that it was isotopically homogeneous, and proposed that the isotopic composition reflected a mixture of weathering inputs from continental and young volcanic components. This homogeneity was confirmed by later studies, leading to the conclusion that the residence time of Sr in the oceans far exceeds the time scales of water mass mixing. The first detailed survey of marine carbonates of Phanerozoic age sketched out the broad outlines of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ variations, identifying periods of radiogenic (high $^{87}\text{Sr}/^{86}\text{Sr}$) compositions in the Carboniferous and late Cenozoic, and relatively nonradiogenic (low $^{87}\text{Sr}/^{86}\text{Sr}$) compositions in the Cretaceous (Peteman et al., 1970). Archean-age carbonates were found to be very nonradiogenic, which was interpreted to indicate minimal input from continental crust, possibly reflecting small continental exposure (Veizer and Compston, 1976). Spooner (1976) made the breakthrough that the nonradiogenic Sr flux was more likely to reflect MOR hydrothermal input rather than erosion of exposed young volcanic rocks. As mass spectrometry precision improved, both broad (Burke et al., 1982; Veizer et al., 1983) and detailed (Hess et al., 1986) Sr isotopic studies of carbonates, including shells and foraminifera, provided a highly resolved Sr seawater curve. This curve has been used for both stratigraphic chronology and to infer changes due to sea-level variations, tectonic activity, weathering, and continental-scale glaciations in the Phanerozoic (DePaolo, 1986; Elderfield, 1986; Raymo et al., 1988).

The Rb-Sr Sr isotope research outlined here provided a broad view of Sr isotope variations in the crust and mantle, and in the last decade, there has been an increase in work on determining $^{87}\text{Sr}/^{86}\text{Sr}$ variations in individual minerals, rather than bulk samples, using in situ approaches, which have included microdrilling, SIMS, and LA-ICP-MS. For example, studies on feldspar phenocrysts in igneous rocks have been used to determine open-versus closed-system behavior in magmatic systems, where both magma recharge and crustal assimilation have been documented from intracrystal variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Davidson et al., 2001; Knesel et al., 1999). In addition, Sr isotope profiles in phenocrysts potentially provide information on crystal residence times when coupled with diffusion modeling across discontinuities (Davidson et al., 2007). In addition to analysis of individual minerals, Sr isotope measurements of melt inclusions document very large $^{87}\text{Sr}/^{86}\text{Sr}$ variations in olivine-hosted melt inclusions from oceanic basalts, which Jackson and Hart (2006) interpreted to reflect mixing of primitive magmas that originated from enriched and depleted mantle reservoirs.

**U-Th-Pb**

The U-Th-Pb system involves decay of three parent isotopes to distinct Pb isotopes: $^{238}\text{U}-^{206}\text{Pb}$ ($t_{1/2} = 4.5$ b.y.), $^{235}\text{U}-^{207}\text{Pb}$ ($t_{1/2} = 0.7$ b.y.), and $^{232}\text{Th}-^{208}\text{Pb}$ ($t_{1/2} = 14$ b.y.). Early efforts on the U-Th-Pb isotope system focused on determining the evolution of the continental crust and mantle, given the framework that Patterson’s (1956) Pb-Pb age of Earth provided. Broad surveys of galena of various ages confirmed that a single-stage growth curve for the crust can explain some data (Kanasewicz and Farquhar, 1965). In contrast, Patterson and Tatsumoto (1964) studied detrital feldspars as a widespread measure of North American continental crust and found that the relatively high abundance of $^{207}$Pb, which can only have been produced early in Earth’s history, required a two-stage growth curve that included an early U/Pb differentiation event between 3.5 and 2.5 Ga, which they interpreted to be the primary formation age for the crust. Armstrong (1968) recognized, as did many others, that the average isotopic composition of modern Pb plotted to the right of the geochron (the Pb-Pb array of the solar system, inferred to include the terrestrial planets), that is, at high $^{206}\text{Pb}/^{204}\text{Pb}$ on a $^{206}\text{Pb}/^{204}\text{Pb}$-$^{207}\text{Pb}/^{204}\text{Pb}$ diagram; this was commonly referred to at the time as “anomalous” or “future” Pb, and it was recognized that this likely required a multistage history of U/Pb evolution. The scope of the Pb isotope mass-balance problem (sometimes referred to as the “Pb paradox”; Allègre, 1968) became clear in studies of basaltic rocks from the ocean basins, where most oceanic basalts lay to the right of the geochron, requiring some sort of multistage history (Gast et al., 1964; Tatsumoto, 1966). An important attempt at solving the “Pb paradox” and the failure of single-stage growth curves came from the “Stacey-Kramers” average crustal growth curve, used to this day, which is a two-stage growth curve that involved a global U/Pb enrichment event at 3.7 Ga, possibly reflecting the first major differentiation event on Earth (Stacey and Kramers, 1975). The “plumbotectonics” model put forth in the late 1970s, and refined in following years, attempted to explain the transport of Pb between the major reservoirs of Earth, and offered a possible explanation to the Pb paradox (Doe and Zartman, 1979; Zartman and Doe, 1981). Moving forward, Pb isotope studies, as well as Sr isotopes, became increasingly integrated with Sm-Nd isotope studies, which provided important breakthroughs in understanding of crust-mantle evolution; these are discussed in the next section.

Recent work on in situ Pb isotope analysis by SIMS and LA-ICP-MS has been applied to subjects ranging from sedimentary provenance to melt inclusions. Pb isotope analyses of single detrital feldspars in both modern (Alizai et al., 2011) and ancient (Tyrrell et al., 2007) sediments have been used to infer paleodrainage configurations, the extent of sediment recycling, and mineral
diagenesis. In situ Pb isotope analyses of feldspar phenocrysts in large caldera-related volcanic systems have shown correlations between the proportion of mantle and crustal components in phenocryst cargos and eruptive frequency and volume (Simon et al., 2007). Initial work on olivine-hosted melt inclusions in oceanic basalt demonstrated very large ranges in isotopic compositions that greatly exceed those measured in bulk samples, and such ranges have been inferred to reflect blending of mantle melts from distinct mantle reservoirs, in addition to wall-rock interactions in the plumbing system (Saal et al., 1998). Later work has suggested less extreme ranges in the isotopic compositions of melt inclusions, but it has also highlighted the utility of in situ isotopic analysis in distinguishing between mantle and crustal processes (Paul et al., 2011).

**Sm-Nd**

Arrival of the Sm-Nd isotope system on the scene in the 1970s opened new research avenues due to the relatively restricted REE variations in a large variety of rocks, as compared to Rb/Sr and U/Pb. The most widely used decay system has been $^{147}$Sm-$^{143}$Nd ($t_{1/2} = 106 \text{ b.y.}$), although the $^{146}$Sm-$^{142}$Nd ($t_{1/2} = 0.1 \text{ b.y.}$) decay system has also been used to trace early solar system processes. A powerful component of the Sm-Nd isotope system was the uniform nature of chondrite meteorites, which reflected generally limited Sm/Nd fractionation (Jacobsen and Wasserburg, 1980), and this led to a reference reservoir, the chondritic uniform reservoir, or “CHUR” (DePaolo and Wasserburg, 1976), which would be used extensively in studies of terrestrial rocks for inferring the time when Nd was extracted from the mantle, an approach that led to the concept of “Nd model ages” (DePaol, 1981a). In western North America, Nd model age variations in a large variety of rocks, as compared to Rb/Sr and Sm/Nd fractionation (Jacobsen and Wasserburg, 1980), and this led to a reference reservoir, the chondritic uniform reservoir, or “CHUR” (DePaolo and Wasserburg, 1976), which would be used extensively in studies of terrestrial rocks for inferring the age of differentiation events. Early work documented a broad anticorrelation between $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd ratios in terrestrial samples (DePaolo and Wasserburg, 1976; O’Nions et al., 1977; Richard et al., 1976), which was recognized as reflecting the distinct time-integrated Rb/Sr and Sm/Nd ratios of “depleted” (high $^{143}$Nd/$^{144}$Nd) and “enriched” (low $^{143}$Nd/$^{144}$Nd) components. For oceanic lavas, this relation was initially termed “the mantle array.” In the three components of Sr, Nd, and Pb isotopes, a “mantle plane” was proposed (Zindler et al., 1982), later modified in multiple component space by the landmark paper by Zindler and Hart (1986), who defined four principal mantle components: a depleted mantle (DMM) anchored by mid-ocean-ridge basalt (MORB), a high $^{206}$Pb/$^{204}$Pb (μ) and high $^{208}$Pb/$^{204}$Pb component (HIMU), defined by ocean-island basalts (OIBs) such as St. Helena, a moderate $^{87}$Sr/$^{86}$Sr and low $^{143}$Nd/$^{144}$Nd enriched component (EM I) represented by Walvis Ridge, and a high $^{87}$Sr/$^{86}$Sr and low $^{143}$Nd/$^{144}$Nd enriched component (EM II), represented by Samoa. It is generally accepted that the DMM component reflects depletion of the mantle through long-term production of continental crust, and the three “enriched” components (HIMU, EM I, and EM II) are generally thought to reflect lithospheric recycling (Fig. 6). Mantle xenoliths from the subcontinental lithospheric mantle demonstrated that the DMM, EM I, and EM II components can be identified in the subcontinental lithospheric mantle for some isotopic systems such as Sr and Nd (Hawkesworth et al., 1990; Menzies, 1989).

Covariation of Sr and Nd isotopes in orogenic arcs showed that many arc lavas were shifted to high $^{87}$Sr/$^{86}$Sr ratios relative to the Sr-Nd mantle array (Hawkesworth et al., 1979). Coupled with new Sr and Nd isotope data from ophiolites that showed strong shifts in $^{87}$Sr/$^{86}$Sr ratios but invariant $^{143}$Nd/$^{144}$Nd during hydrothermal alteration at MORs (McCulloch et al., 1981), preferential shifts in $^{87}$Sr/$^{86}$Sr in orogenic arcs were interpreted to reflect a subduction component derived from the altered slab. A landmark study by Hildreth and Moorbath (1988) proposed that mixing, assimilation, storage, and homogenization of arc magmas extensively occurred in the lower crust during ponding of mantle-derived basaltic magmas near the Moho, a model known as “MASH,” and one that still provides a framework for arc magmatism. The relative coherence of Sm/Nd ratios during melting provided a means of seeing through recent magmatic events to infer the time when Nd was extracted from the mantle, an approach that led to the concept of “Nd model ages” (DePaol, 1981a). In western North America, Nd model age
provinces correlated with Archean, Proterozoic, and Phanerozoic crustal boundaries and allowed identification of older Nd components in granitic batholiths (Bennett and DePaolo, 1987; Farmer and DePaolo, 1983). Neodymium isotope data from large caldera complexes from North America, however, identified large proportions of mantle, indicating that such complexes represented new periods of net crustal growth (Johnson, 1991), suggesting that ignimbrites may contain a larger proportion of mantle than granitic rocks, and hence periods of net crustal growth (Johnson, 1993).

The Nd model age concept has been extensively applied to fine-grained sedimentary rocks, and for samples that had depositional ages younger than 2 Ga, Nd model ages were usually older than 2 Ga, indicating that most Phanerozoic- and Proterozoic-age sedimentary rocks have been recycled from older sources (Allègre and Rousseau, 1984; Goldstein et al., 1984; O’Nions et al., 1983). An exception is sedimentary rocks that were deposited at the same time as orogenic episodes, which were found to contain a larger proportion of mantle Nd than nonorogenic sediments, reflecting net crustal growth (Michard et al., 1985). Mass growth distributions for the continents calculated from Nd crustal residence times using sedimentary rocks indicated that ~40% of the present-day continental mass formed by 3.8 Ga (Jacobsen, 1988), a conclusion that is similar to that inferred from Pb isotope compositions of detrital feldspars, as discussed earlier (Patterson and Tatsumoto, 1964). A critical component to extracting crustal growth curves from Nd model ages, however, is quantifying the extent of crustal recycling in sediments (Allègre and Rousseau, 1984); as will be seen later herein, significantly different crustal growth curves have been inferred using Hf isotope data.

In contrast to Sr, the residence time of Nd in seawater is very short, on the order of 10$^2$ as, and early researchers in Sm-Nd isotopes recognized that this should make the isotopic composition of Nd in seawater a sensitive indicator of local input (Piepgras and Wasserburg, 1980; Piepgras et al., 1979). This early work, which confirmed the isotopic provinciality of Nd in seawater, and hence its use as a sensitive tracer of water masses, was later extended back in time through analysis of Fe-Mn crusts and authigenic marine sediments. Examples include tracing the distinct evolution of the Pacific-Panthalassa and Iapetus Oceans from the Neo- proterozoic to present (Keto and Jacobsen, 1988), and closure of the Central American isthmus that restricted water mass communication between the Pacific and North Atlantic Oceans (Burton et al., 1997). In addition to Nd, Pb isotope studies of Fe-Mn sediments demonstrated that Pb isotopes were also provincial, commensurate with the short residence time for Pb in seawater (Abouchami and Goldstein, 1995).

Advances in mass spectrometry in the 1990s allowed application of the 146Sm-142Nd isotope system, which requires measurement of 142Nd/144Nd ratios to a very high precision of several parts per million. The short half-life of the 146Sm-142Nd system provides a sensitive tracer of processes in the first few hundred million years of solar system history. Harper and Jacobsen (1992) demonstrated an average 142Nd/144Nd enrichment of 32 ppm for rocks from the 3.8 Ga Isua supracrustal belt, Greenland, relative to average terrestrial rocks. Consideration of coupled 142Nd/144Nd and 143Nd/144Nd variations suggested that the 142Nd enrichment recorded Sm/Nd fractionation in the source reservoir(s) of the Isua rocks likely occurred between 4.55 and 4.45 Ga. These results were confirmed by Bennett et al. (2007), who interpreted the 142Nd enrichment to record early mantle differentiation in the first 30–75 m.y. of Earth’s history. Boyet and Carlson (2005, 2006) compared high-precision 142Nd/144Nd data from meteorites and a wide variety of terrestrial mantle–derived rocks and documented that chondrite meteorites have 142Nd depletions on the order of 20 ppm relative to the average of terrestrial rocks, and they suggested that this records a major mantle differentiation event ~30 m.y. after Earth formation. Moreover, Boyet and Carlson proposed that there is a missing low-142Nd/144Nd reservoir in Earth, possibly located at the base of the mantle, assuming that Earth formed with a chondritic Sm/Nd ratio. Carlson and Boyet (2008) suggested that the missing reservoir, which should have enriched incompatible trace-element contents, reflects high-density components that settled into the deep mantle from an early terrestrial magma ocean. Evidence for an incompatible element–enriched mafic crust very early in Earth history lies in rocks from the Nuvvuagittuq greenstone belt, Canada, which has relatively low 142Nd/144Nd ratios that overlap those of chondrites, and which has a 146Sm-142Nd “age” of ca. 4.3 Ga (O’Neil et al., 2008). A contrasting view of the “missing 142Nd reservoir” is offered by Jacobsen et al. (2008), who argued that the difference in 142Nd/144Nd ratios between terrestrial rocks and chondrite meteorites may be explained by isotopic heterogeneity during Earth’s accretion, rather than invoking a missing reservoir in Earth’s mantle.

$^{179}$Lu-$^{176}$Hf

The isotope $^{179}$Lu decays to $^{176}$Hf with a half-life of 37 b.y. The large Lu/Hf fractionations that are produced by garnet, as well as the high abundance of Hf in zircon, have long spurred interest in this analytically difficult isotope system. A series of pioneering papers in the 1980s outlined the range in Hf isotope compositions of meteorites, mantle-derived rocks, crustal zircons, and sedimentary rocks (Patchett et al., 1981; Patchett and Tatsumoto, 1980; Patchett et al., 1984). Hf and Nd isotope compositions for OIB are broadly correlated, but Hf and Nd isotopes for MORB are not correlated. Early work on zircons from igneous and metamorphic rocks as old as 3.7 Ga suggested a chondritic Hf evolution for the crust until ca. 2.8 Ga, at which time high initial $^{176}$Hf/$^{177}$Hf ratios appeared, indicating the presence of a globally differentiated mantle (Patchett et al., 1981). Later work on detrital zircons indicated the presence of a depleted mantle by 3.0 Ga (Stevenson and Patchett, 1990). Detailed studies of the Hf isotope compositions for the oceanic mantle identified HIMU, EM I, and EM II components defined by Sr-Nd-Pb isotope studies (Salters and Hart, 1991), but Hf isotopes require two DMM components, one of which has high $^{176}$Hf/$^{177}$Hf ratios that requires garnet as an important ancient component in the source regions of MORB (Salters, 1996).
The late 1990s saw a marked increase in Lu-Hf research as MC-ICP-MS instruments became widespread. High-precision Hf isotope measurements of juvenile crystalline rocks, as well as ancient sediments, initially documented a limited range in initial \(^{176}\text{Hf}/^{177}\text{Hf}\) ratios prior to 3.0 Ga, which stood in contrast with Sm-Nd isotope data that suggested very large ranges in initial \(^{143}\text{Nd}/^{144}\text{Nd}\) early in Earth’s history (Vervoort and Blichert-Toft, 1999; Vervoort et al., 1999), although later work, based on detrital zircons (see following), has since expanded the Hf isotope database for Precambrian rocks by several orders of magnitude and documented a much larger range in initial \(^{176}\text{Hf}/^{177}\text{Hf}\) ratios. High-quality MC-ICP-MS data for OIBs identified subtle variations in Hf-Nd isotope arrays that provided strong support for an ancient subduction of pelagic sediment that was previously hypothesized but difficult to confirm using TIMS data (Blichert-Toft et al., 1999).

A major effort in combined U/Pb geochronology and Hf isotope studies of detrital zircons, using in situ analysis methods, began in the early 2000s and has continued to the present. Much of this work has been aimed at addressing the growth and evolution of continental crust, given the wide variety of crustal growth histories that have been proposed (e.g., Allegre and Rousseau, 1984; Armstrong, 1981; Condie, 1998; Hurley and Rand, 1969; Taylor and McLennan, 1985). U/Pb zircon geochronology has long highlighted major peaks in crystallization ages at ca. 2.7 and ca. 1.8 Ga, as well as other peaks in more detail (e.g., Condie, 1998), leading a number of workers to conclude that crustal growth has been episodic (e.g., Rino et al., 2004). This in turn has led to models where catastrophic events in the mantle have been invoked to explain punctuated periods of very rapid crustal growth. In contrast, the distributions of Hf isotope model ages for detrital zircons do not show the strong peaks recorded in U/Pb ages, which suggests that the U/Pb age record may reflect biases in preservation rather than periods of episodic crustal growth (e.g., Belousova et al., 2010; Hawkesworth et al., 2009, 2010; Voice et al., 2011). Recognizing that Hf isotope model ages in detrital zircons may reflect mixtures of mantle-derived and recycled components, Kemp et al. (2006) combined U/Pb geochronology and O and Hf isotopes to separate a recycled high-d\(^{18}\text{O}\) sedimentary component from juvenile, mantle-derived components that reflect net addition to the continents. This approach has forced a major change in thinking about crustal growth rates based on detrital zircons, and it suggests that as much as 70% of current continental crustal volume was produced by 3 Ga, followed by slower, but relatively uniform, rates of crustal growth since that time (Dhuime et al., 2012).

Looking at the oldest detrital zircons, the Archean and Hadean zircons from the Jack Hills, Australia, have been a logical target of Lu-Hf studies. Early work on mineral separates by Amelin et al. (2000, 1999) highlighted the difficulty in interpreting both Lu-Hf and U-Pb data from complex zircons, and they found little evidence for enriched or depleted components at 3.8 Ga, suggesting minimal differentiation on Earth by this time. Later work by Harrison et al. (2005) reported remarkably positive \(\varepsilon_{\text{Hf}}\) values up to +13 at 4.3 Ga, obtained by in situ methods using LA-MC-ICP-MS, and they argued that an active plate-tectonic system existed at this time. Valley et al. (2006) noted that significant errors could be introduced in calculating initial \(\varepsilon_{\text{Hf}}\) values given the complexity of the zircons and the disparate volumes involved in U-Pb (SIMS) and Lu-Hf (LA-MC-ICP-MS) measurements. Harrison et al. (2008) combined Pb and Lu-Hf analysis to constrain \(^{207}\text{Pb}/^{206}\text{Pb}\) ages to the same ablated volume analyzed for Lu-Hf, and this revised approach found only negative \(\varepsilon_{\text{Hf}}\) values down to −5 at 4.2 Ga. Recently, Kemp et al. (2010) reported LA-MC-ICP-MS Pb and Hf isotope analyses that produced negative \(\varepsilon_{\text{Hf}}\) values between 3.9 and 4.3 Ga in age (Fig. 7), which they argued reflects only small domains of enriched (low Lu/Hf) components in primitive crust, and not widespread melting and depletion of the mantle, nor an active plate-tectonic system prior to 4 Ga.

**Re-Pt-Os**

Radiogenic Os isotope studies have generally focused on the \(^{187}\text{Re}-^{187}\text{Os}\) system \((t_{1/2} = 42 \text{ b.y.})\), although the \(^{190}\text{Pt}-^{186}\text{Os}\) system \((t_{1/2} = 489 \text{ b.y.})\) has also been explored. The Re-Pt-Os isotope system differs greatly from the radiogenic systems discussed previously in that these elements are siderophile/chalcophile (Shirey...
and Walker, 1998), and the major inventories exist in Earth’s core, distantly followed by the mantle (see previous discussion). Work on this analytically challenging system, which began in the 1980s, showed that the mantle has remained relatively nonradiogenic, lying within the range of chondritic meteorites, but the very high Re/Os ratios of continental crust produced very high $^{187}$Os/$^{188}$Os ratios over time (Allègre and Luck, 1980; Luck and Allègre, 1983). Correlations between Os and O isotopes in OIBs have been interpreted to reflect ancient subducted sediments (Lassiter and Hauri, 1998), or assimilation of hydrothermally altered oceanic crust during ascent of magmas to the surface (Gaffney et al., 2005). In contrast, Escrig et al. (2005) interpreted high $^{187}$Os/$^{188}$Os ratios at Pogo Island to record assimilation of lower continental crust during opening of the Atlantic Ocean.

The large Re/Os fractionations that are produced during melting of peridotite have been used to trace the evolution of the lithospheric mantle. Walker et al. (1989) first proposed this approach for cratonic peridotite xenoliths, where they calculated Os model ages that reflect Re depletion “events” that may record the time of stabilization of the lithospheric mantle. Compilations of Os isotope data from both whole-rock samples and sulfides from cratonic peridotite xenoliths commonly show very nonradiogenic $^{187}$Os/$^{188}$Os ratios that may be interpreted as Re depletion ages between ca. 2.5 and 3.0 Ga (Carlson et al., 2011) recently reported high $^{187}$Os/$^{188}$Os ratios in sulfide inclusions in diamonds of 3 Ga age or younger, which they interpreted to reflect eclogites that originated as subducted oceanic crust that became incorporated in the subcontinental lithospheric mantle.

Radiogenic (high) $^{187}$Os/$^{188}$Os ratios in orogenic arc lavas have been interpreted in two ways. Some workers have inferred such compositions to reflect subducted sediments (Alves et al., 1999, 2002), although other workers have argued that the low Os content of crustal material is unlikely to shift the Os isotope compositions of the subarc mantle, instead interpreting the radiogenic Os isotope compositions as reflecting assimilation of young, mafic lower crust (Chesley and Ruiz, 1998; Hart et al., 2003; Jicha et al., 2009). The importance of the second interpretation lies in the potential ability of the Re-Os isotope system to trace interaction with arc crust, which is essentially invisible using other isotopic systems such as O, Sr, Nd, Hf, and Pb isotopes, and which has implications for estimating net crustal growth in orogenic arcs.

Turning to the very long-lived $^{190}$Pt-$^{186}$Os system, Walker et al. (1995) first proposed that core material might be identified in OIBs, often suggested to reflect mantle plumes that originate at the core-mantle boundary (e.g., Hawkesworth and Schersten, 2007). Brandon et al. (1999, 2000) observed correlated enrichments in $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os in modern OIBs that they interpreted to represent a high-$^{190}$Pt component from the core, and later work on Archean komatiites identified similar features (Puchtel et al., 2005). Alternative proposals for correlated $^{186}$Os/$^{188}$Os and $^{187}$Os/$^{188}$Os in OIBs include Pt- and Re-rich materials that could reflect ancient crustal components, or ancient pyroxenite in the mantle, although Brandon and Walker (2005) suggested that such materials are unlikely to be common components in OIBs. Recently, Luguet et al. (2008) documented $^{186}$Os enrichments in pyroxenites, eclogites, sulfides, and Pt-rich alloys in peridotites, providing support for the argument that $^{186}$Os may not be a unique tracer of core components in OIBs.

**ORGANIC GEOCHEMISTRY: INVESTIGATING CARBON COMPOUNDS PRESERVED IN ROCKS**

The past 50 yr have witnessed exponential growth in our appreciation of the ubiquity and diversity of organic compounds that are preserved in sediments and sedimentary rocks. A number of these substances, or their derivatives formed through diagenetic alteration processes, were discovered in sediments before they were recognized as natural products in living organisms (Ourisson and Albrecht, 1992; Ourisson et al., 1979). Technological innovation combined with the quest for an understanding of fossil fuel composition, formation, and occurrence were the initial drivers of research on sedimentary organic matter in the 1960s and 1970s (Kvenvolden, 2006). As the possibility of gaining evolutionary insights by way of “molecular paleobiology” became more clear, the driving force for organic geochemistry shifted (Eglinton, 1970; Peterson et al., 2007). In more recent times, it has been recognized that organic molecules in the air, in water, and in sediments carry in their chemical structures and stable isotopic compositions a myriad of environmental and climate signals. Investigating these records on both human and geologic time scales has now become the prime focus of research in organic geochemistry (Eglinton and Eglinton, 2008; Gaines et al., 2009).

**The Quest to Understand the Origins of Petroleum and Other Fossil Fuels**

The invention of computerized mass spectrometers, in combination with high-resolution capillary gas chromatography, was a critical early technical development, and this led to the discovery that petroleum was composed of thousands of discrete organic compounds. In the 1960s, geochemists working in the fossil fuel industry, in collaboration with academic scientists, also demonstrated that sedimentary kerogen and bitumen, the precursors of petroleum, could be correlated to commercial deposits of oil and gas using combinations of organic compound distributions and isotopic patterns (Hunt et al., 2002; Peters et al., 2005). They also convincingly demonstrated that buried organic matter was predominantly of biological origin (e.g., Hills and Whitehead, 1966), and that progressive changes in its chemical
composition correlated with burial depth and geothermal heating rates, thereby providing a tool with which to assess the nature and distribution of coal, petroleum source rocks, and natural gas (Seifert and Moldowan, 1980, 1978). Transport of organic matter in clays opened a new mechanistic understanding to its preservation and accumulation in source rocks, and a way in which organic carbon burial could be understood in the context of the principles of sequence stratigraphy (Creaney and Passe, 1993; Hedges and Keil, 1995).

Diagenetic processes, mediated by microbes, water, and reduced sulfur compounds, render complex biomolecules into both simpler hydrocarbons and much more complex material (kerogen) through polymerization and cross-linking (Adam et al., 1993; Kohnen et al., 1989). Integration of geochemical understanding with sedimentary geology and basin modeling ultimately resulted in a more informed understanding of hydrocarbon systems, including resource and risk assessment (Hunt, 1996; Tissot and Welte, 1978).

Development of Molecular Paleontology

Paleontologists have long recognized that microbial life has dominated life on Earth for most of its history, yet microscopic fossils comprise an infinitesimally small fraction of the biomass that has been present on Earth, and the vast majority of microbes leave no visible trace at all. It was recognized early, however, that microbial lipids derived from their cell walls, membranes, and pigments are preserved, and, in fact, form the dominant organic molecules that can be found preserved in sedimentary rocks. In Figure 8, we summarize some of the important organic molecules used in geochemistry, organized according to contemporary molecular phylogeny. The concept of “biomarker chem stratigraphy” has emerged as a means for using these molecules to chart evolutionary innovation, mass extinctions and radiations, chemical events in the ocean, and climate change (Gaines et al., 2009). For example, the rise of complex multicellular life in the Neoproterozoic, the transitions in ocean plankton through the Phanerozoic, and the advent and radiation of land plants are among a few of the biological innovations that have been, and continue to be studied using biomarkers.

After several decades of study, it is now clear that major paleontological mileposts are accompanied by corresponding biosynthetic innovations that are recorded in molecular fossils. Colonization of the continents by plants, for example, was enabled by invention of a range of structural biopolymers, including lignin and cellulose. Plants built defenses against desiccation and predation utilizing cuticles made of waxy hydrocarbons for the former, and an array of sesqui- (C_{15}), di- (C_{20}), and triterpenoids (C_{30}) and resinitic compounds for signaling and for warding off insect predators. Distinct differences in the chemical defenses utilized by conifers (Gymnosperms) and flowering plants (Angiosperms) can be recognized through the presence of distinctive diterpenoids in Paleozoic and early Mesozoic rocks and petroluems (e.g., Noble et al., 1985). An increase in the prevalence of triterpenoids is now known to be associated with the increased abundance of flowering plants in the late Mesozoic and Cenozoic (Moldowan et al., 1994; Murray et al., 1998; Simoneit et al., 1986). Recently, it has become clear that biogeo graphical aspects of plant occurrence and dispersal are reflected in sedimentary hydrocarbons (Dutta et al., 2011). In the marine realm, micropaleontology informs us that the Paleozoic dominance of green and red clades of planktonic algae gave way to the modern dominance of chlorophyll a + c plankton, an observation that is directly correlated with the prevalence of their respective steroidal and acyclic isoprenoidal hydrocarbons in marine sediments and oils (e.g., Knoll et al., 2007; Rampen et al., 2007; Sinninghe Damsté et al., 2004; Volkman, 2003). A practical application of the evolution of complex organisms and changes in the composition of ocean plankton through time has been development of age-diagnostic biomarkers that can place constraints on the timing of deposition of petroleum source rocks (e.g., Grantham and Wakefield, 1988; Holba et al., 1998).

As with studies of algae, sensitive GS-MS (gas chromatography–mass spectrometry) methods developed in the last few decades have provided the means with which to study biomolecules that are unique to animal phyla. Cholesterol is the predominant membrane sterol of animals, and there is little else in the way of other preservable molecules that could constitute a robust “metazoan” biomarker. Basal invertebrate phyla, defined as those least removed from their single-celled ancestors, include sponges, cnidarians, and echinoderms, and these are the exceptions in that they have a wealth of complex biochemistries, possibly reflecting defenses against predation. Demosponges are well known for their biosynthetic capacity to produce distinctive terpenoids, including sterols that have a rare 24-isopropylcholestan skeleton (Bergquist et al., 1991). 24-Isopropylcholesterol have been found in the calcisponges, hexactinellid sponges, or choano flagellates, and these form a unicellular sister group to sponges (Love et al., 2009). Hydrocarbon derivatives of the distinctive C_{30} sponge sterols are prevalent in sedimentary rocks and petroleums of Cryogenian (Neoproterozoic) to Early Cambrian age, and they are thought to reflect an acme in the abundance of demosponges in sedimentary environments of this time (Love et al., 2009; McCaffrey et al., 1994). The molecular fossil record suggests that demosponges made their first appearance in the Cryogenian, and this is concordant with molecular clock estimates of metazoan divergence times (Peterson et al., 2007).

It is now recognized that biomarker hydrocarbons can be diagnostic for certain kinds of paleoenvironmental circumstances (Fig. 9). Water-column redox stratification, elevated salinity, marine versus nonmarine sedimentation, and clastic versus carbonate environments are some of the conditions that can be encoded into fossil hydrocarbon distribution patterns. A prime example lies in the insights provided by organic geochemical proxies into biogeochemical processes occurring during oceanic anoxic events (OAEs), and especially those associated with mass extinction events. The work of Holser and others (Holser, 1977; Holser et al., 1989) first recognized
shifts in the isotopic compositions of C, O, and S in marine sediments, interpreted to record the disruption of ocean chemistry and consequent biological mass extinction. Biogeochecists have subsequently observed concomitant signals in organic molecules, redox-sensitive trace elements, and other geochemical proxies. One recurring trend is seen in the prevalence of biomarkers derived from the green sulfur bacteria (Chlorobi) in sediments that were deposited during OAEs. Chlorobi are anoxygenic phototrophs that use sulfide as an electron donor for photosynthesis, and these produce distinctive light-harvesting carotenoid and chlorophyll pigments that may be recorded in preservable structural features (Grice et al., 1996; Sinninghe Damsté and Koopmans, 1997; Summons and Powell, 1987). Diagenetic reduction and stabilization of these compounds are enhanced under the strongly reducing (euxinic) conditions that are favored by the green sulfur bacteria.

Figure 8. A “tree of life,” based loosely on the nucleotide sequences of small subunit ribosomal ribonucleic acid (RNA), to illustrate life’s three domains and the diverse structures of lipids that are characteristic of organisms at the domain level and, in some cases, phylum level. For example, most eukaryotes utilize sterols, and, in a few cases such as diatoms, dinoflagellates, and demosponges, there are particular sterols that are very specific. The membrane lipids of bacteria and eukaryotes incorporate hydrocarbon chains that are linear or branched in relatively simple ways, and these are mostly linked to glycerol via ester linkages. Archaea, on the other hand, build equivalent structures using isoprenoidal chains, and they are linked to glycerol with ether bonds. Many of these features are preservable and can be observed in organic matter extracted from sedimentary rocks. Improved understanding of the way in which lipid chemistry relates to physiology, phylogeny, and environment, and deduction of the pathways by which organic molecules become preserved in sediments have been prime accomplishments of organic geochemists in the past 50 yr. GDGT—glycerol dibiphytanyl glycerol tetraethers.
Geologists and paleontologists have long debated the origin of the Permian-Triassic extinction, both the cause and the biological response, and work in molecular paleontology in the last decade has provided important insights. Studies of a core drilled into the end-Permian type section at Meishan, China, show that Chlorobi carotenoids are particularly abundant throughout the last few million years of the Permian and into the Early Triassic, implying that shallow-water euxinic conditions were protracted at the type section of the greatest mass extinction of the geological record (Cao et al., 2009; Grice et al., 2005). Examination of other Permian-Triassic transition sections confirms the pattern and suggests that euxinic conditions were pervasive globally, as far as can be discerned from continental margin sediments of the Tethys, Panthalassic, and Boreal Oceans (Hays et al., 2007, 2012). These observations are consistent with other isotopic and inorganic proxies for a global and intense oceanic anoxic event during the Permian-Triassic transition. Independent modeling also suggests that toxic hydrogen sulfide would have been upwelling from the deep ocean onto continental shelves and entering the atmosphere (Kump et al., 2005), implying that sulfide toxicity was a contributing factor to the biological mass extinction in the marine realm as well as on land. Co-occurring with the evidence for euxinia, molecular fossils shed light on other aspects of this event, including transitions in ocean plankton (Cao et al., 2009), and a massive terrestrial weathering event (French et al., 2012; Sephton et al., 2005; Xie et al., 2007).

Although many theories abound, no consensus has been reached on the processes that instigated the end-Permian mass extinction (Erwin, 2006). Evidence that the event had its roots in ocean chemistry is consistent: Anoxia with accompanying effects of hypercapnia, ocean acidification, and sulfide toxicity could all have contributed to the loss of marine life, and, arguably, to loss of life on land (Holser, 1977; Knoll et al., 1996; Twitchett et al., 2001; Wignall and Hallam, 1992). Numerous researchers also point to volatile release during emplacement of the Siberian Traps lavas and intrusions (Payne and Clapham, 2012). These authors argued that gases liberated during the volcanism itself, augmented by additional C and S volatiles released from affected sediments, can account for most of the end-Permian palaeontological and geochemical observations, and this is consistent with
the timing and tempo indicated by the most recent geochronological studies (Kamo et al., 2003; Mundil et al., 2010; Shen et al., 2011). Despite continued debate on the ultimate trigger, most authors agree that the geochemical and geologic evidence for a bolide impact (Becker et al., 2001) is unclear (Farley and Mukhopadhyay, 2001). In this context, it is also noteworthy that the organic geochemical signals that accompany the Cretaceous–Paleogene impact and mass extinction event bear no resemblance to those seen at OAEs (Sepulveda et al., 2009).

There are other examples where biomarker research in the last 20 yr has helped us to understand oceanic anoxia. The chlorobri carotenoid signal is one of several organic geochemical features that are consistently observed during intervals of enhanced black shale deposition during the Paleozoic and Mesozoic Eras (Koopmans et al., 1996; Pancost et al., 2004). Isorenieratane, chlorobactane, and the aryl isoprenoids derived from them, along with C, S, and N isotopes and other biomarker anomalies that are indicative of anoxia, euxinia, and water-column stratification, comprise a recurring signal that is seen in both clastic and carbonate sediments deposited during Mesozoic OAEs (Kuyper et al., 2004; Schouten et al., 2000). Many of these sediments, such as the Kimeridge Clay Formation, are also prolific source rocks for petroleum deposits that carry the same signal (Van Kaam-Peters et al., 1998a, 1998b). The prevalence of organic-rich and petroleum-prone sediments that were deposited during the Mesozoic Era comprises the bulk of the world’s oil-in-place inventory, reflecting pervasive development of narrow rift basins and seaways, greenhouse conditions, and sluggish ocean circulation during breakup of the Pangean supercontinent (Klemme and Ulmishek, 1991).

Studies of molecular fossils in Precambrian sedimentary rocks have been pursued in earnest since the 1980s, and this work has shown that such rocks exhibit an array of novel molecular and isotopic features that are not seen in younger sedimentary sequences (Grantham and Wakefield, 1988; Grosjean et al., 2009; Klomp, 1986; Summons et al., 1988). Unprecedented distributions of steroids, for example, can be traced to the proliferation of green and red algae, as well as sponges, and this accords with other geochemical evidence for the Neoproterozoic oxygenation of the atmosphere and ocean (Canfield et al., 2007; Fike et al., 2006) and paleontological evidence of the proliferation of complex life (Erwin et al., 2011; Knoll et al., 2004). Euxinic conditions have been inferred from geochemical studies of Neoproterozoic strata, and this is reflected in carotenoid molecular fossil distributions in the same rocks (Brocks et al., 2005). Steroid and triterpenoid hydrocarbons have also been recovered from much older rocks (Dutkiewicz et al., 2006; George et al., 2008; Waldbauer et al., 2009). Some of this work has been challenged on the basis of C isotope data obtained by nano-SIMS (Rasmussen et al., 2008), suggesting that the recovered biomarkers instead reflect contamination. In contrast, studies of fresh drill cores recovered from the Kaapvaal craton that were targeted to address this issue (Waldbauer et al., 2009) suggest that complex terpenoids, and particularly the steroids, could be indigenous to the samples and represent compounds that were biosynthesized prior to the Great Oxidation Event (GOE) at ca. 2.3–2.4 Ga. The presence of steroids in older than 2.5 Ga rocks supports a raft of isotopic and trace-element proxies, some of which have been discussed already, which indicate that trace amounts of oxygen were being produced (e.g., Anbar et al., 2007; Czaja et al., 2012) and respired (Eigenbrode and Freeman, 2006) in the surface oceans well in advance of the GOE. Further drilling, using ultraclean drilling protocols and contamination tracers, is currently under way in the Pilbara craton, Australia, and this is expected to shed further light on ocean-atmosphere redox conditions in the Neoproterozoic.

**Elucidating Paleoenvironmental Records**

One of the most important discoveries in organic geochemistry in the last 50 yr has been the recognition of some classes of organic molecules that encode signals for past climate regimes. Of key importance are the proxies for sea-surface temperature (SST) based on the degree of unsaturation in long-chain ketones (C_{37}, alkenones) from marine algae (the Uk37 index; Brassell et al., 1986), and the proportions of isoprenoidal ether lipids (dubbed glycerol dibiphytanyl glycerol tetraethers or GDGT) derived from archaea (the Tex86 index; Schouten et al., 2002). In soils and paleosols, bacterial (non-isoprenoidal) ether lipids have been proposed to provide information on both temperature and pH (Weijers et al., 2006). Significant effort has been expended in elucidating the specific organisms responsible for these proxies, as well as the physiological basis of the sedimentary temperature records that are encoded by alkenones and ether lipids. In the case of the former, prominent marine haptophyte algae such as *Isochrysis galbana*, *Emiliania huxleyi*, and *Gephyrocapsa oceanica*, living primarily in the surface mixed layer and sometimes extending to the thermocline (Ohkouchi et al., 1999), are widely recognized as the primary biological sources in the oceans (Volkman et al., 1995, 1980). Given the biogeographical trends and temperature preferences of alkenone-producing algae, it appears likely that the alkenones record lipids that were derived from a combination of cold- and warm-water adapted strains. Nutrient status, salinity, growth rate, growth stage, and temperature all influence the distributions of alkenones in cultured haptophytes, yet empirical calibrations of the Uk37 indices to core tops, and to cultures, appear to be very robust over a wide range of temperatures, environmental variables, and spatial scales (Prah et al., 2003; Rosell-Melé et al., 1995; Sikes and Volkman, 1993). The C_{37} alkenones occur in sediments that predate the appearance of contemporary alkenone-producing haptophytes, and, because of their apparently close evolutionary relations and similarity to fossil forms, this has potentially opened application of the proxy to ancient sedimentary records on multi-million-year time scales. Paleotemperature reconstructions into deep time, however, will have to be viewed cautiously until more is known about the physiological function of C_{37} alkenones in haptophyte algae. What is most impressive about the alkenone SST records is the degree of concordance with independent isotopic records, including
O isotope variations recorded in ice cores and foraminifera (e.g., Herbert et al., 2001). It has become clear that multiple approaches are needed to understand and constrain each proxy in terms of the robustness of paleotemperature records and the effects of lateral sediment redistribution (Mollenhauer et al., 2011).

In contrast to the alkenones and their sedimentary records as expressed in Uk37 data, the temperature proxy based on archaeal ether lipids (Tex86) is less well constrained with respect to the precise sources of the isoprenoidal GDGTs and the controls on their production. The Tex86 proxy emerged from the discovery of abundant archaeal plankton communities that populate oceans, lakes, and other aquatic environments, in addition to recognition that membrane-spanning GDGTs contain variable numbers of cyclopentane rings that could be isolated from particulate organic matter and the underlying sediments (Delong et al., 1998). A particular problem, however, is that diverse Crenarchaeota and Euryarchaeota that inhabit both the water column and the sediments produce some of the same compounds that comprise the proxy. In addition, other studies show that the prevalence, and production, of GDGT often takes place at great depth (Ingalls et al., 2006; Sinninghe Damsté et al., 2002), frequently near or within oxygen minimum zones. Nevertheless, evidence suggests that the distributions of GDGT in core-top sediments are similar to those of (epipelagic) marine Crenarchaeota living in the top 100 m of the water column, an observation consistent with the relatively robust core-top calibrations of SST with Tex86 (Wuchter et al., 2005). Numerous studies point to an origin for archaeal ether lipids in ammonia-oxidizing Marine Group I Crenarchaeota (Schouten et al., 2008). Evidence has been presented to show that Tex86 values agree with foraminifer proxies that indicate rapid ocean warming during the late Paleocene thermal maximum (Zachos et al., 2006). Paleotemperature records extending into Mesozoic time are considered possible (Schouten et al., 2003), but there are few avenues available for independent verification. An important consequence that flows from the discovery of isoprenoidal GDGT has been the realization that the Crenarchaeota are exceptionally important components of the marine carbon and nitrogen cycles (Delong, 2009; Ingalls et al., 2006).

Using Stable Isotopes to Better Understand the Origins of Biomarkers

One of the continuing challenges of organic geochemistry has been to determine the sources of individual biomarker molecules, because few compounds are thought to exclusively derive from a single organism or represent a single biogeochemical process. Sterols, for example, are made or used by almost all eukaryotes, from microbes to mammals. Despite their varied chemical structures, sterols are not as diverse as the taxonomic distributions that they represent. One way to constrain the origins of molecules is through their stable isotope compositions. Initial work used bulk measurements (e.g., Hare et al., 1991), but a desire for improved specificity and precision drove development of tools that allow isotopic measurements at the molecular level using continuous-flow approaches that were analogous to GC-MS and LC-MS (liquid chromatography–mass spectrometry; see also previous discussion). Carbon was the first and most obvious element targeted for compound-specific isotope analysis (CSIA), and the initial results immediately revealed the diverse origins of sedimentary organic molecules (Freeman et al., 1990; Hayes et al., 1990). Analogous methods for H (Sessions et al., 1999), N (Macko et al., 1997), and S (Amrani et al., 2009) soon followed. It is now common to measure multiple isotopic compositions of individual compounds such as chlorophylls, as well as the porphyrins and maleimides that are derived from them (Chikarai et al., 2005). In turn, the technical capability to make precise isotopic measurements on these elements exposed the dearth of knowledge about the ways in which these biosynthetic processes, organismic physiology, and environmental parameters influence the isotopic abundances of individual molecules (Hayes, 2001; Laws et al., 1997, 1995; Popp et al., 1998; Sessions et al., 1999; Smith and Freeman, 2006). The impact of developing and perfecting tools and techniques for compound-specific isotope analyses has been profound. The protocols and logic are now routinely used in archaeology, paleoclimatology, paleohydrology ecology, and forensics, and geochemists have been the instigators of many of these applications (Lichtfouse, 2000).

Radiocarbon measurements of individual organic molecules have also led to new insights into the age structure of fossil lipid assemblages, and their transport from source to sedimentary sinks (Pearson et al., 2001). Thus, in contemporary environmental settings, it is possible to discern the age relations of multiple paleoclimatic proxies (Mollenhauer et al., 2003), thereby resolving processes such as winnowing and lateral advection of organic matter (Kusch et al., 2010; Mollenhauer et al., 2011). The robustness, scope, and fidelity of organic SST proxies based on algal alkenones and archaeal ether lipids have been significantly increased through knowledge gained from compound-specific radiocarbon measurements (Eglinton and Eglinton, 2008).

Which Organisms Produce All These Sedimentary Lipids?

As interest turned to understanding the origins and diagenetic pathways by which organic molecules became fossilized, there was a great expansion in our knowledge of the diversity of lipids in sediments before, in fact, their biological precursors were identified in living organisms (Ourisson et al., 1979; Rohmer, 2010; Rohmer et al., 1980). The emergence of another analytical tool, high-performance liquid chromatography coupled to mass spectrometry (HPLC-MS), enabled identification of increasingly large and complex polar lipid molecules such that, today, geochemists have focused on tracking the distributions of membrane-spanning lipids (Schouten et al., 2000a), intact polar lipids (Sturt et al., 2004), and complex biohphanoids (Talbot et al., 2008) from organisms through the water column and into sediments. Intact polar lipids can be proxies for living organisms and, often in combination with deoxyribonucleic acid (DNA), have been used to map out biogeochemical processes
in sediments (e.g., methanotrophy; Orphan et al., 2002) and the water column (e.g., Sinninghe Damsté et al., 2005), as well as to help define the extent of the deep subsurface biosphere (Lipp et al., 2008; Rütters et al., 2002).

Advances in identification of the diverse types of organic molecules in rocks have been concomitant with efforts to increase our understanding of the ways in which organisms produce these lipids (biosynthetic pathways), the evolution of these pathways, and the array of functions performed by lipid molecules in cells (physiological roles). This is one of the current frontiers of organic geochemistry, because, very often, the taxonomic relations are often ambiguous between molecules of interest in the environment or rock record and their precursor organisms. Based on knowledge derived from cultured taxa, we know that hopanoids, for example, are distributed very unevenly across the bacterial domain, but the reasons for this remain mysterious (Rohmer et al., 1984). Precisely how key compounds are produced is only now coming to light, and efforts to deduce this have led to the discovery of a completely unknown isoprenoid biosynthesis pathway in bacteria (Rohmer, 2003; Rohmer et al., 1993); such findings can have societal implications because they may lead to new classes of antibiotics. The revolution in genomics has, therefore, given geochemists a new tool for identification of lead to new classes of antibiotics. The revolution in genomics provides fundamental constraints on the evolution of the biosynthetic pathways used by life.

**Extinct Radionuclides and Early Solar System Chronology**

Extinct radionuclides that were present in the solar nebula have decayed away, but their presence can be inferred from their radiogenic daughter isotopes. The first extinct radionuclide found in meteorites, $^{129}$I, was discovered in 1961, and others followed in the next 50 yr. Additional extinct nuclides are now recognized to have been present in the solar nebula, including $^{10}$Be, $^{26}$Al, $^{41}$Ca, $^{55}$Mn, $^{60}$Fe, $^{107}$Pd, $^{146}$Sm, and $^{182}$Hf. In some cases, extinct radionuclides can provide high-resolution chronometers for early solar system events (Nyquist et al., 2009). The $^{146}$Sm-$^{142}$Nd system has already been discussed here in regard to early terrestrial rocks.

One of the most useful extinct nuclides is $^{26}$Al, which decays to $^{26}$Mg with a half-life of ~730,000 yr. Its former existence was first proven when Lee et al. (1977) analyzed plagioclase and other minerals in a refractory Ca-Al inclusion (CAI) from the Allende meteorite, and they determined that plagioclase had a large $^{26}$Mg excess (relative to nonradiogenic $^{26}$Mg). Because CAIs are the oldest solar system materials, based on their $^{207}$Pb-$^{208}$Pb ages, their $^{26}$Al contents are taken to reflect those at the beginning of the solar system, and other measurements are compared to the $^{26}$Al/$^{27}$Al ratio and $^{207}$Pb/$^{208}$Pb age of CAIs for chronology. The $^{26}$Al value reflects production by stellar nucleosynthesis, and its occurrence in the solar nebula is commonly attributed to “seeding” by a nearby supernova. Refinements in SIMS and ICP-MS techniques have permitted measurements of $^{26}$Al-$^{26}$Mg systematics in samples that have low Al contents, including chondrules and differentiated meteorites. An example is illustrated in Figure 10, which shows different $^{26}$Al/$^{27}$Al ratios for chondrules in several classes of chondrites, and this implies that chondrules formed several million years after CAIs.

The $^{182}$Hf-$^{182}$W system, with a half-life of 8.9 m.y., has also proved to be very useful in dating early solar system events. Early measurements by N-TIMS (negative thermal ionization mass spectrometry) were difficult, but this chronometer was made truly accessible when MC-ICP-MS analysis became available (Halliday et al., 1996). Both Hf and W are refractory elements and so usually occur in chondritic proportions. Because, however, Hf is lithophile and W is siderophile, the $^{182}$Hf-$^{182}$W system can date metal-silicate fractionation events such as core formation. Such ages, in turn, constrain the time of planet accretion. For example, the estimated age of Earth’s accretion (50% mass), based on this chronometer, is 30 to >100 m.y. after CAIs (Halliday, 2004). More rapid accretion ages for asteroidal bodies were determined by Kleine et al. (2009).
Nebular Condensation

Many, although not all, of the solids that now comprise solar system bodies once condensed from nebular vapor. Early attempts to determine the condensation sequence in a cooling gas of solar composition involved simple calculations, performed long before digital computers were available. The equilibrium condensation behavior of elements in a nebular gas was rigorously modeled by Grossman and Larimer (1974) and other workers since then (e.g., Petaev and Wood, 1998). The canonical condensation sequence, showing condensing phases and the fraction of each element condensed at various temperatures, is illustrated in Figure 12. Based on experimental determinations of entropy, enthalpy, and heat capacity, equations of state describing the thermodynamic stabilities of a host of possible minerals under various conditions can be calculated. Liquids are not stable at the low pressures appropriate for the solar nebula. Some minerals in the condensation sequence do not condense directly, but form or adjust their compositions by reactions of previously condensed phases with the gas. This condensation calculation was done for the 23 elements with the highest cosmic abundances. Generally, thermodynamic data for trace elements are lacking, so chemical analyses of trace elements in high-temperature minerals of chondritic meteorites guide our understanding of their condensation behavior. Accordingly, in these models trace elements are allowed to condense as simple metals, oxides, or sulfides, which are assumed to dissolve into appropriate major mineral phases. The validity of condensation calculations has been supported by studies of refractory inclusions (CAIs) in chondrites, which have bulk chemical compositions consistent with those calculated for the first 5% of condensable matter (Davis and Richter, 2004). Moreover, the same minerals that comprise these inclusions are predicted to have been the earliest condensed phases (Fig. 12). There remains some controversy, however, about whether the CAIs are actually condensates or refractory residues from evaporation (the reverse of condensation).

Condensation calculations have also been done at different nebular pressures and using nonsolar gas compositions (Ebel and Grossman, 2000; Wood and Hashimoto, 1993; Yoneda and Grossman, 1995). Parts of the solar nebula may have been enriched in dust, which, when vaporized, could have yielded nonsolar vapor, possibly allowing more reduced phases or even liquids to condense. These condensation calculations could also apply to other stars, e.g., red giants, which can have nonsolar compositions.

Organic Matter from Space

The molecular and isotopic chemistry of extraterrestrial organic matter is another area where technical innovation has spurred improved appreciation for the nature and diversity of organic compounds formed in the interstellar medium and the processes that alter them prior to their delivery to Earth in meteorites (Derenne and Robert, 2010) and interstellar dust particles (Flynn et al., 2004). The low-molecular-weight compounds...
identified include many classes of biologically important molecules, for example, amino acids (Kvenvolden et al., 1970), hydroxyacids and dicarboxylic acids (Cronin et al., 1993; Lawless et al., 1974; Peltzer et al., 1984), as well as nucleobases (Martins et al., 2008). Isotopic data and pyrolysis studies suggest that distinct processes are involved in formation of small molecules and macromolecular material (Sephton et al., 2004; Yuen et al., 2008). Perhaps the most profound, enigmatic, and controversial finding was that some amino acids were not racemic, as had long been considered fact (Engel and Macko, 1997; Engel et al., 1990; Engel and Nagy, 1982). This discovery, originally dismissed as due to terrestrial contamination, became accepted once it was demonstrated also to be a feature of some nonpro-

Figure 11. Oxygen isotopes (relative to SMOW) measured in Ca-Al inclusion (CAI) from a carbonaceous chondrite define a mass-independent fractionation trend, distinct from the terrestrial mass-dependent trend. Figure is modified from Clayton et al. (1973). SMOW—standard mean ocean water.

tein amino acids (Cronin and Pizzarello, 1997). Moreover, the L-enantiomeric excess of some compounds such as isovaline in the Murchison and Orgueil meteorites appears to be related to the extent of aqueous processing, suggesting that it could reflect amplification of a small initial isovaline asymmetry. If correct, this would be inconsistent with the theory that ultraviolet (UV) circularly polarized light was the primary source of L-enrichment in amino acids. It seems possible, therefore, that early life on Earth had access to molecular building blocks with the left-handedness that characterizes the amino acids of all life today (Engel and Macko, 2001; Glavin and Dworkin, 2009). Such results demonstrate the importance of “off-world” geochemistry to informing us about terrestrial evolution.

Lunar Geochemistry

The Moon is a geochemical experiment conducted under vastly different conditions than Earth. The geochemical exploration of the Moon began with the return of samples by Apollo astronauts in 1969, which extended over an exciting 4 yr period. Depletions in volatile elements and enrichments in refractory elements measured in these rocks support the giant impact hypothesis for the Moon’s formation (Taylor et al., 2006). Vaporization of portions of the target (Earth) and the impactor, followed by incomplete condensation in Earth orbit, can account for the fractionation observed in volatile and refractory elements. Measured depletions of siderophile elements in lunar rocks are consistent with models that indicate preferential incorporation of the silicate mantles of the impactor and target into the Moon, accompanied by accretion of the impactor’s core into Earth’s core.

The revelation that a magma ocean once existed on the Moon (Wood et al., 1970) has profoundly changed planetary science, and now wholesale melting has been proposed for a number of bodies, including early Earth. REE analyses came of age during

Figure 12. A model of the condensation sequence for a cooling gas of solar composition at $10^{-4}$ atm pressure. Condensed minerals are labeled in italics, and curves show the fraction of each element condensed as a function of temperature. REE—rare earth element. Figure is modified from Grossman and Larimer (1974).
the Apollo program, as discussed earlier, and the complementary REE patterns of anorthosite from the highlands crust and basalts from the maria (Fig. 13) provide the most persuasive evidence for a lunar magma ocean (Taylor and Jakes, 1974). In this model, the thick anorthositic crust was formed by flotation of plagioclase, which produced a positive Eu anomaly in the crust, and this was balanced by the Eu depletion that was produced by olivine and pyroxene that accumulated to form the mantle, a characteristic that was inherited by later mare basalt melts. The Eu anomaly in lunar rocks was enhanced by the Moon’s low oxidation state, that was inherited by later mare basalt melts. The Eu anomaly produced by radioactive decay or by reactions initiated by cosmogenic rays. Orbital measurements provide global coverage and thus are particularly useful in understanding geochemical processes at a planetary scale. Global maps of the distribution of Fe and Th, which are particularly sensitive to this technique, have been employed to distinguish lunar terranes based on their geochemical characteristics (Jolliff et al., 2000). The petrology of each terrane has been interpreted unambiguously by comparison with the Fe and Th contents of returned lunar samples. Other results, made possible by measuring the neutron flux from the surface, included the discovery of H at the lunar poles associated with cold, permanently shadowed craters believed to contain water ice (Feldman et al., 2001).

The Mars Exploration Rovers Opportunity and Spirit carried Alpha Particle X-Ray Spectrometers (APXS) that analyzed the chemical compositions of hundreds of rocks and soils on the surface of Mars (Brückner et al., 2008; Gellert et al., 2006). By measuring characteristic X-rays produced by alpha particles and X-rays emitted from a radioactive source, the APXS was able to analyze all of the major elements and a few minor and trace elements. These studies were a critical part of the classification of rocks encountered during rover traverses, and they provided constraints on the processes that formed these materials. Opportunity analyzed sedimentary rocks that contained high contents of S, Cl, and Br, interpreted to reflect evaporation of salt-laden brines, demonstrating that liquid water was once abundant on Mars (Squyres et al., 2004). On the other side of the planet, Spirit analyzed a variety of ancient basaltic rocks (Fig. 14) that have compositions that are distinct from those of younger Martian basaltic meteorites, buttressing the argument that although heterogeneous, Mars is fundamentally a basalt-covered world (McSween et al., 2009).

Stardust in the Laboratory

Tiny motes of stardust, condensates that formed around dying stars or farther out in the interstellar medium, were discovered in chondritic meteorites (Lewis et al., 1987), after a long search beginning in the 1960s. These diamond nanoparticles were isolated by dissolving chondrites in a series of harsh acids, and at each step tracking the isotopically anomalous Xe they contained. The grains are thought to have been implanted when the outer layers of giant C-rich stars were sloughed off and condensed as diamond, and were subsequently implanted with distinctive nuclides produced when the star exploded as a supernova. Approximately 20 types of presolar grains, including silicon carbide (Tang and Anders, 1988) and graphite (Amari et al., 1990), as well as oxides, nitrides, and silicates, have now been found. All are distinguished by their exotic isotopic compositions (Tang and Anders, 1988).

The challenging elemental and isotopic analyses of stardust grains, which range from a few nanometers to a few micrometers in size, illustrate the great progress made in micro-analytical techniques. An example, using SIMS-analyzed C and N isotopes to fingerprint the sources of presolar silicon carbide grains, is
shown in Figure 15. More importantly, the isotopic compositions of presolar grains provide “ground truth” for stellar nucleosynthesis models, directly linking cosmochemical measurements in the laboratory to astrophysical theory. These data also (1) provide information on capture cross sections for neutrons, the capture of which makes heavier elements, (2) demonstrate where theoretical models are inadequate to describe the internal structures of stars, (3) identify neutron sources for the s-process, and constrain the scale of mixing in supernovae (Nittler, 2003; Zinner, 2004). Presolar grains also fundamentally changed the way we think about the solar system’s formation. Their widespread occurrence in primitive meteorites demonstrates that a hot nebula did not vaporize all preexisting solids, overturning a view that prevailed 50 yr ago.

INTEGRATING THE PICTURE: GEOCHEMICAL CYCLES

The concept of geochemical cycles dates to the late nineteenth century and was well established (i.e., began to appear in textbooks) by the mid-twentieth century (e.g., Goldschmidt, 1954). The modern phase of quantifying global geochemical cycles arguably dates from the pioneering work of Garrels and Mackenzie (1971, 1972), who integrated major-element chemistry (including C, S, and Cl) into a steady-state recycling model for the evolution of the sedimentary mass. As described in greater detail in the following, geochemical cycles are often complex and inter-related, and considerable effort has been directed toward trying to understand how cycles are linked. Many elemental cycles require monograph-length treatment, and the fact that there is a journal devoted solely to biogeochemical cycling (Global Biogeochemical Cycles) reflects the sustained interest in geochemical cycles.

In geochemical cycles, the reservoirs (mass, M) and fluxes of individual elements (or groups of closely related elements) into and out of the system (mass/unit time, \( F_{\text{in}} \) and \( F_{\text{out}} \)) are quantitatively accounted for over geological time \( t \). Accordingly, assessments of geochemical cycles are essentially a mass balance of the element of interest on some appropriate physical scale over some appropriate duration, and to a great extent are the natural consequence of quantifying the overall rock cycle (Gregor, 1992) and hydrological cycle (Fig. 16). Geochemical cycles are considered to be either “exogenic,” for those operating on or near Earth’s surface (hydrosphere, atmosphere, biosphere ± sediments), typically on relatively short time scales (<~10^4–10^7 yr), or “endogenic,” for those operating within the interior of Earth (oceanic and continental crust, mantle, core ± sediments), typically on relatively long time scales (>~10^7–10^10 yr). The physical interface between the endogenic and exogenic parts of an element’s geochemical cycle typically occurs in soils and the sedimentary cover. Characterization of complete global cycles requires integration of both endogenic and exogenic cycles as witnessed, for example, by the relatively recent recognition that the C cycle is...
affected by significant levels of microbial activity deep within parts of Earth’s crust (e.g., Hazen et al., 2012), in addition to mantle sources.

Depending on the way in which the physical and/or temporal scales are defined, geochemical cycles may be either open or closed, where the distinction is a function of whether or not external inputs and/or outputs take place within the defined reservoirs. Those concepts govern whether or not a geochemical cycle is in steady state (i.e., $dM/dt = 0; F_{\text{in}} = F_{\text{out}}$), leading to the further concept of residence time ($\tau = M/F$), which in turn is equivalent to the inverse of the first-order rate constant ($\tau = 1/k$) for simple linear cycles, thus providing information about the response times (i.e., kinetics) of the system (Lasaga and Berner, 1998).

One problem that attracted early attention was the issue of elemental cycling through the oceans. This interest was initiated largely by the pioneering work of Sillén (1961), who demonstrated that seawater chemistry could be in a steady-state condition, controlled by equilibrium reactions between atmospheric gases and marine carbonate and silicate minerals. Up until the early 1950s, the conventional wisdom was that the oceans’ salt had accumulated over the entirety of geological time. During the 1960s–1980s, considerable effort went into determining the apparent mean oceanic residence times of the elements ($\tau$), a concept first introduced by Barth (1952), as well as documenting the balance between the masses of the various elements that entered the oceans from rivers, and those exiting the oceans through sedimentation (e.g., Drever et al., 1988). The ensuing research identified important additional sources of elements to the oceans (e.g., basalt-seawater hydrothermal interaction) that had not been previously recognized, additional reservoirs for elements (e.g., pore waters, altered basalts, estuaries, continental shelves), and numerous mineral and biogeochemical reactions, leading to a far more complete understanding of marine chemistry (e.g., Broecker and Peng, 1982).

By evaluating geochemistry in the framework of geochemical cycles, the fundamental processes that influence elemental distributions (geological, geophysical, chemical, biological, temporal) are better addressed (Lerman and Wu, 2007). A good example of the value of this approach in identifying previously unrecognized processes and reservoirs is the well-known “missing sink” issue for carbon (Broecker, 2012). During the 1990s, the short-term (exogenic) C cycle had been quantified sufficiently
to recognize that ~15%–20% of the CO₂ delivered to the atmosphere by fossil fuel combustion could not be accounted for by the recognized major C reservoirs (atmosphere, accounting for ~50%, and seawater, accounting for ~30%–35%). This led to a major research effort to identify the missing sink, which in turn resulted in recognition of the terrestrial biosphere (previously considered relatively minor) as a major reservoir for exogenic C.

**The Biological Connection**

The importance of biological activity in controlling the cycling of a wide range of elements has been long appreciated (e.g., Vinogradov, 1943). Attempts, however, to both define and quantify global biogeochemical cycles involving elements that are essential for biological activity have only occurred somewhat recently, though they are of great geochemical interest (e.g., Garrels and Lerman, 1981). Biogeochemical cycles consider some or all of a wide array of biologically relevant elements in an integrated manner, including those that are a significant part of living tissue and skeletons (C, O, H, N, P, S, Ca, Si), those that may be less involved in living matter but are important in redox processes allowing for energy transfer (Fe, Mn, in addition to N and S), and a long list of minor and trace elements that may be necessary for metabolism (e.g., biolimiting) and/or substitute for major elements of biogeochemical importance (e.g., Fe, Mn, Mg, Ba, Ge, B, Mo, V, Zn, and even the REEs).

The C cycle (and its role in biogeochemical cycles) is of intrinsic interest to geochemists due to the role of C in all biological activity and its importance in the geological record as a common rock-forming constituent (limestone, dolomite, carbonaceous sediment) and as a natural resource (fossil fuels). The fact, however, that C has received by far the most attention of any of the geochemical cycles, and indeed may be the most intensely studied geochemical problem of the past 50 yr and more (Berner, 2004; Broecker, 2012; Des Marais, 2001), is mainly due to the observation that atmospheric CO₂ concentrations have systematically risen since the industrial revolution at a rate that is unprecedented for the Phanerozoic, due mainly to the burning of fossil fuels (Fig. 17). It is now widely recognized that perturbations within the C cycle (temporal variations in atmospheric CO₂) represent a dominant control on the changes of Earth’s current climate, as well as both short-term and long-term paleoclimate. The recent abrupt increase in atmospheric levels of this important greenhouse gas, due mainly to human activity, is also now understood to play a central role in influencing recent global climate change and increases in mean global surface temperatures (Berner, 2003).

**Redox Processes in Biogeochemical Cycles**

The recent focus on element cycling, including biogeochemical cycles, is primarily driven by redox chemistry, both abiologic or biologic, due to its importance in controlling the composition and evolution of the ocean-atmosphere system (e.g., Raiswell and Canfield, 2012). As discussed already, C is certainly the most studied redox-sensitive element that is cycled between reduced and oxidized forms today on Earth, driven largely by photosynthesis. This in turns drives atmospheric O₂ contents through the extent of C burial and thus plays a central role in the long-term O cycle. This influences, for example, the long-term cycling of Fe, one of the most important redox elements in rocks, given its high abundance in the terrestrial planets. The redox couple with Fe was studied extensively in the 1970s, with a major focus on banded iron formations (BIFs), and later, the relation between the Fe biogeochemical and marine evolutions. Evaluation of the geochemical cycles of redox-sensitive trace elements such as Cr and Mo rose in prominence in the 1980s and 1990s.

One of the major issues addressed in studies of redox biogeochemical cycling over the past 50 yr has been the history of atmospheric O₂ over geological time (Holland, 1962). As briefly noted already, a prominent approach to understanding the history of atmospheric O₂ on Earth has been study of both mass-dependent and mass-independent fractionation (MIF) of stable S isotopes, and these records are compared, along with C and Fe isotopes, in Figure 18. The range in d³⁴S values for sulfides in marine sedimentary rocks generally increases with decreasing age, an observation that has also been long recognized (e.g., Canfield, 2001). The general increase in the highest d³⁴S values measured for sulfides is broadly taken to record an increase in the d³⁴S values of seawater sulfate, and a recent compilation of this can be found in Canfield and Farquhar (2009). It is almost universally accepted that the range in d³⁴S values for sulfides

![Figure 17](image-url)
Figure 18. Temporal variations in (A) banded iron formation (BIF) deposition and atmospheric oxygen, (B) δ13C values of Ca-Mg carbonates, (C) δ34S values for sulfides, (D) mass-independent S isotope fractionation, expressed as Δ33S, and (E) δ56Fe values; δ56Fe values are broken out as black shales (high-S, high-C contents), Ca-Mg carbonates, and BIF samples. Green band represents period of maximum BIF deposition and immediately predates the increase in atmospheric oxygen contents. BIF deposition is from Bekker et al. (2010). Atmospheric O2 curve is from Catling and Claire (2005), shifted to older ages based on disappearance of mass-independent S isotope fractionation (Farquhar et al., 2010). Early pulses of O2 time band are based on previous studies (Anbar et al., 2007; Czaja et al., 2012; Duan et al., 2010; Kendall et al., 2010; Voegelin et al., 2010). The δ13C data are from Shields and Veizer (2002). The δ34S data for sulfides and seawater sulfate are from Canfield and Farquhar (2009), and Δ33S values for sulfides are from the same source. The δ56Fe values are from sources cited in Johnson et al. (2008b), with additional data sources (Czaja et al., 2010, 2012; Heimann et al., 2010; Hoffmann et al., 2009; Planavsky et al., 2009; Steinhoefel et al., 2009; Tsikos et al., 2010; Valaas-Hyslop et al., 2008; Von Blanckenburg et al., 2008). All isotopic data reflect bulk sample analyses.
reflects various extents of bacterial sulfate reduction (Canfield, 2001, 2005). Turning to S-MIF, nonzero $\delta^{34}S$ values for marine sedimentary rocks are restricted to samples of ca. 2450 Ma age and older, and most studies interpret this to indicate very low atmospheric oxygen contents (originally discovered by Farquhar et al. [2000a], and recently reviewed by Farquhar et al. [2010]), although alternative explanations have been proposed (discussed earlier herein). The transition from large $D^{33}S$ values to zero $D^{33}S$ values at ca. 2450 Ma correlates with an increase in the range of $d^{34}S$ values, consistent with an increase in seawater sulfate contents and development of free oxygen in the atmosphere, which in turn would enhance rates of bacterial sulfate reduction (Canfield, 2005; Farquhar et al., 2011).

As discussed earlier, the $d^{34}C$ values for Ca-Mg carbonates of Archean and Proterozoic age largely scatter closely about zero, with the exception of the 2.3–2.0 Ga Lomagundi excursion (Fig. 18). Increased organic C burial seems the most likely explanation for the increase in $d^{34}C$ values for carbonates at this time, which in turn would drive further increase in atmospheric $O_2$. This would tend to increase seawater sulfate contents, providing opportunities to increase the $^{34}S/^{32}S$ fractionations produced by microbial sulfate reduction due to “excess” sulfate; this would increase the inventory of sedimentary sulfides that have very negative $d^{34}S$ values (Fig. 18). Accompanying the rise in atmospheric $O_2$ would be a loss of S-MIF, reflected in a shift toward zero $D^{33}S$ values for sulfides younger than 2.3 or 2.4 Ga in age (Fig. 18).

The largest Fe isotope excursion known in the rock record occurs in the Neoarchean and Paleoproterozoic (Fig. 18). Because the vast majority of Fe in the crust has a $\delta^{56}Fe$ value near zero, including low-C, low-S sedimentary rocks that have Fe contents similar to those of the average crust (e.g., Johnson et al., 2008b), deviations in the $\delta^{56}Fe$ values from zero are significant and generally rare in terms of the Fe mass balance of Earth. The zero to positive $\delta^{56}Fe$ values for rocks older than 3.5 Ga in age, which to date mainly include BIFs, are generally accepted to reflect partial oxidation of marine hydrothermal Fe$_{aq}$, suggesting that the amount of oxidant was limited (Dauphas et al., 2004), and recent Fe isotope work suggests that photic zone $O_2$ levels were <0.001% of present day at this time (Czaja et al., 2013). More controversial, however, is the strong decrease in $\delta^{56}Fe$ values between ca. 3 and 2.5 Ga. Rouxel et al. (2005) and Anbar and Rouxel (2007) proposed that oxidation of marine hydrothermal Fe$_{aq}$ during BIF genesis, or oxide precipitation on continental shelves, produced negative $\delta^{56}Fe$ values in seawater, which was directly incorporated into sulfide-rich marine sedimentary rocks. As recently discussed by Czaja et al. (2012), extensive oxidation of Fe$_{aq}$ is a likely explanation for the low $\delta^{56}Fe$ values of Neoarchean Ca-Mg carbonates and, in fact, provides one of several lines of evidence for intermittent oxygenation of surface environments in the time leading up to the Great Oxidation Event (GOE) at ca. 2.3 or 2.4 Ga (Anbar et al., 2007; Kendall et al., 2010; Voegelin et al., 2010). Oxidation of Fe$_{aq}$, however, cannot easily explain the spread in $\delta^{56}Fe$ values for Fe-rich rocks such as BIFs, and Yamaguchi et al. (2005) and Johnson et al. (2008a, 2008b) do not generally interpret the Fe isotope compositions of such lithologies to be a direct proxy for seawater, instead favoring microbial Fe cycling as an explanation for the Fe isotope variability.

The relative paucity of highly negative $\delta^{56}Fe$ values after the GOE (Fig. 18) has been interpreted to reflect a decrease in the footprint of microbial Fe$^{3+}$ reduction as microbial sulfate reduction increased in its impact on redox cycling. Sulfate reduction would produce abundant sulfide, which readily reacts with Fe$^{3+}$ oxides, decreasing Fe$^{3+}$ availability to microbial reduction. The increase in $\delta^{56}Fe$ values that generally corresponds with a decrease in BIF deposition (Fig. 18) is consistent with a transition from an Fe-dominated redox cycle before the GOE to a S-dominated redox cycle after the GOE. Collectively, the temporal record of BIF deposition and C, S, and Fe isotopes displays remarkable coherence that can be well explained by expected changes in microbial redox cycling during the transition from an anoxic to oxic world.

We close by considering redox cycling on another planetary body. The recent phase of Mars exploration has led to recognition of a long-lived dynamic sedimentary cycle on that planet. This has generated interest in characterizing geochemical cycles and evaluating the implications for surface processes (e.g., Grotzinger et al., 2011), an interest that undoubtedly will increase with the successful landing of the Mars Science Laboratory. Mars may represent a valuable end member for understanding near-surface geochemical cycles in general due to the absence of plate tectonics. There appears to be a long-term evolution of sedimentary mineralogy, where a common occurrence of Noachian (older than 3.7 Ga) clay minerals gives way to a sulfate-rich mineralogy in the Hesperian (ca. 3.7–3.2 Ga), and finally to anhydrous ferric oxides in the Amazonian (younger than 3.2 Ga; Bibring et al., 2006). Recent work on the ALH84001 meteorite has provided support for clay minerals on the surface of Mars prior to 4.0 Ga (Beard et al., 2013). As on Earth, where sedimentary mineralogy (e.g., BIF) provides a proxy for geochemical evolution (Hazen et al., 2008), this secular change in sedimentary mineralogy has been interpreted to represent acidification, oxidation, and desiccation of the Martian surface over geological time. Although the current atmosphere is very thin, most models call for a more substantial early Martian atmosphere that was dominated by CO$_2$. Sulfur, however, is also enriched in Mars surficial deposits, and it now appears that some form of a S-cycle may have strongly influenced surficial processes over much of geological time, leading to widespread low pH conditions (Halevy et al., 2007; King and McLennan, 2010; McLennan, 2012).

CONCLUDING REMARKS

We are not so bold as to predict what advances will occur in geochemistry in the next 50 yr, as we are quite sure that many of the analytical and computational gains that have been key factors to a number of geochemical advances were not envisioned by geochemists in the early 1960s. It was also probably not clear to these geochemists what the impact of plate tectonics would
be, or of obtaining samples from the Moon, or of in situ analyses of rocks and soils on Mars. In a shorter time frame than five decades, however, it seems likely that the trend toward interdisciplinary research, where multiple large data sets are brought to bear on geologic problems, is likely to expand. In addition, there will likely be huge gains in computational and data storage capacity, although analytical advances may be more muted, given the fact that many analyses are now limited by counting statistics rather than electronics, although there is certainly room for large improvements in terms of sampling efficiency of many instruments (what gets to the detector versus what is consumed).

A major unknown for the future of geochemistry, and of science in general, is the commitment to research by broader society, and such issues will undoubtedly affect what is written in a similar paper in the early 2060s.

ACKNOWLEDGMENTS

We thank the organizing committee of the 125th anniversary celebration of the Geological Society of America for the opportunity to write this summary of progress in geochemistry. Johnson and Summons acknowledge support from the National Aeronautics and Space Administration (NASA) Astrobiology Institute during the time this review was prepared. McLennan acknowledges support from NASA’s Cosmochemistry Program. We thank Richard Carson, Robert Clayton, John Hayes, Scott Samson, John Valley, and Richard Walker for helpful reviews of the manuscript.

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Five decades of advances in geochemistry


MANUSCRIPT ACCEPTED BY THE SOCIETY 11 FEBRUARY 2013

Printed in the USA