GEOCHEMISTRY

1. Introduction

Geochemistry is the chemistry of the natural environment and it encompasses the earth as well as other Solar System bodies, what Antoine Lavoisier described as "the grand laboratory of nature." A complete definition might be that geochemistry applies chemistry to understanding the earth and its cosmic environment and using that understanding to better the human condition. Because it's the planet we have the most data on and, more importantly, it's the one we inhabit, most of geochemistry focuses on the earth. Nevertheless, because the earth formed in the same process as the rest of the Solar System, it must be considered in the context of that system.

Indeed, one of the objectives of geochemistry is to understand the earth's formation four and one-half billion years ago and how it has evolved and continues to evolve from its initial, still poorly understood state. Earth's evolution began with an early differentiation into a dense, iron-rich core and a silicate mantle surrounded by a tenuous (in comparison to the massive outer planets) atmosphere. That evolution continues as geologic processes ranging from the hydrologic cycle to volcanism and plate tectonics continually shuffle chemical elements between various geochemical "reservoirs" such as the crust, the oceans, the atmosphere, and the mantle. Geochemistry attempts not only to define the compositions of these reservoirs but also to understand the processes occurring within and between them.

Understanding how elements are reshuffled between reservoirs of course helps us understand fundamental geologic processes. For example, the telltale signature of marine sediments is present in the composition of lavas erupted by volcanoes overlying subduction zones such as Mt. St. Helens in the Cascades or Pinatubo in the Philippines. That in turn reveals that material from the earth's surface can be carried to depths of 100 km or more where the mantle is melting beneath these volcanoes. Over Earth's history, carbon has been shuffled between the deep Earth, the oceans, the atmosphere, sedimentary rocks, and the biosphere. We now recognize that shuffling carbon, in the form of CO_2, in and out of the atmosphere has been an important control on climate over that history (1–3). Merely redistributing carbon between the oceans and atmosphere has been a key factor in amplifying the effects of small variations in the earth's orbit and rotation into the large climatic swings of the Pleistocene Ice Ages (4,5). Some of the CO_2 transformed to organic matter by phytoplankton and then to petroleum by geologic processes has been civilization's primary energy source since the Industrial Revolution. Some elements, such as gold and platinum are incredibly scarce in the earth's crust, in part because most of the earth's inventory is sequestered in its core. Nevertheless, hydrothermal and volcanic processes have occasionally produced deposits, "ores," enriched in these elements many orders of magnitude over their abundances in the earth's core or iron meteorites (which are the remnants of asteroidal cores).

The practical value of geochemistry derives from understanding the processes that produce these resources: knowing how they form greatly aids mineral exploration to insure a continuous supply. On the other hand, resource exploitation, use, and disposal have their costs to the environment and human health and

DOI: 10.1002/0471238961.koe00029

happiness. We need to know the "natural" level of toxins, for example, lead in water or mercury in seafood, to identify man-made pollution and Understanding how toxic substances such as lead, mercury, cadmium, and hydrocarbons behave in the natural environment is critical to maintaining a habitable environment.

2. Origins

The term "geochemistry" was coined in 1838 by the German-Swiss chemist Christian Friedrich Schönbein, better known as the discoverer of ozone, who wrote, "In a word, a comparative geochemistry ought to be launched, before geognosy can become geology, and before the mystery of the genesis of our planets and their inorganic matter may be revealed" (6). The roots of geochemistry are, however, much older and intimately intertwined with the roots of chemistry, both of which were nurtured in the fertile soil of alchemy and metallurgy. The goal of alchemy was, after all, to transform one naturally occurring substance to another, such as gold. Even as chemists came to recognize that there were certain fundamental substances, elements, that could not be so transformed and sought to identify these elements, it was in natural substances that they sought them. So, for example, in 1755 the Scottish chemist Joseph Black recovered magnesia (MgO) from dolomite and recognized magnesium as an element, and Humphry Davy identified calcium as an element in 1808 after isolating it from limestone.

Gustav Bischof's 4-volume *Lehrbuch der chemischen und physikalischen Geologie* (7) is arguably the first geochemistry textbook. Among other things, Bischof emphasized the importance of water in what we would call today "geochemical cycles" and understood that water chemistry reflected weathering reactions with the rocks through which it flowed. As chemists of the late nineteenth and earlier twentieth centuries such as Maxwell, Gibbs, Arrhenius, Lewis, and Randall laid the foundations of chemical thermodynamics and kinetics, geochemistry evolved from a descriptive to a quantitative science.

The foundations of modern geochemistry were laid in the late nineteenth and early twentieth century by three individuals in particular, F. W. Clarke in the United States of America, Victor Goldschmidt in Norway and Germany, and Vladimir Vernadsky in Russia. F.W. Clarke (1847–1931), who spent most of his career as chief chemist of the U.S. Geological Survey, made a number of remarkable contributions to both chemistry and geochemistry, and served as the president of the American Chemical Society in 1901. His classic work "The Data of Geochemistry" (8), of which there were several editions, summarized current knowledge of the composition of the earth and its various components such as igneous and sedimentary rocks and mineral springs. Victor Goldschmidt (1888–1947) was one of the first to apply the thermodynamic principles developed by J. Willard Gibbs and others to understanding the origin and evolution of rocks. If one were to put an exact date on the birth of modern geochemistry, it would 1922 when Goldschmidt published papers on the differentiation of the earth from an early homogeneous body to one with an atmosphere and hydrosphere, crust, mantle, and core (9). By considering their properties and in which phases they occurred in meteorites, Goldschmidt divided the elements into atmophile (eg, N, He), lithophile (eg, Mg, Si, O), siderophile (eg, Ni, Co, Au), and chalcophile (eg, Zn, Pb)

(Figure 1**a**) and argued that the first three groups were concentrated in the atmosphere–hydrosphere, the crust and mantle, and the core, respectively, as a consequence of this differentiation. Goldschmidt's classification, as it is known, is still used by geochemists today, although with some caveats: elements

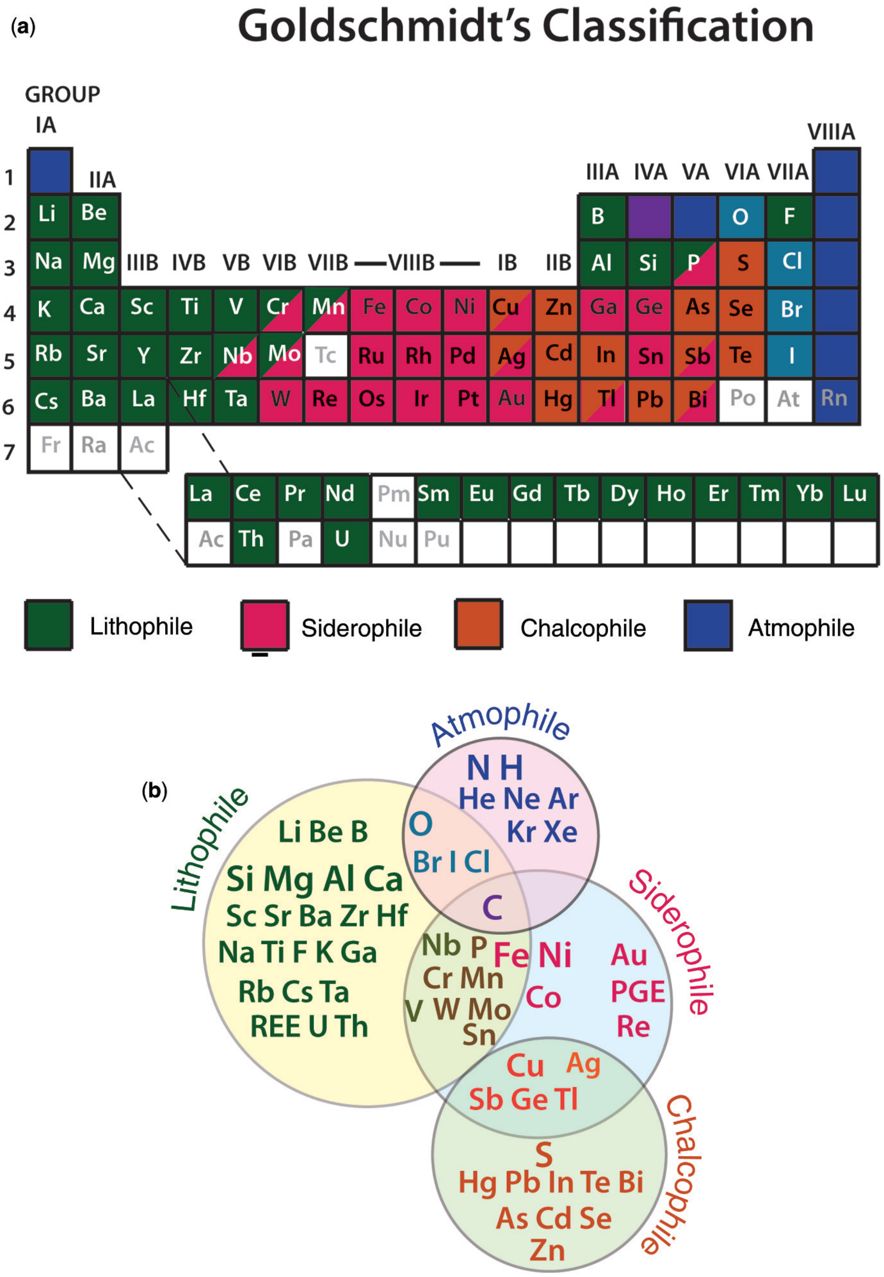

Fig. 1. Goldschmidt's classification of the elements: lithophile: partition into oxides and silicates; siderophile: partition into metal; chalcophile: partition into sulfides; atmophile: condense at low temperature or partition into aqueous solutions.

concentrated in the earth's hydrosphere are included with the atmophile group and the behavior of some elements can be complex and depend on factors such as pressure, oxygen and sulfur fugacity, etc (Figure 1**b**); consequently, many chalcophile elements are concentrated in the earth's core. Goldschmidt went on to make many other fundamental contributions in geochemistry, mineralogy, chemistry, and physics.

Meanwhile in Russia, the Ukrainian-Russian mineralogist Vladimir Vernadsky (1863–1945) was laying the foundations of biogeochemistry. In his concept of the biosphere (10), Vernadsky emphasized that life itself is a geological force that can shape the earth, a view perhaps controversial at the time but now accepted. Together, Clarke, Goldschmidt, and Vernadsky are considered the founders of modern geochemistry.

The founding of the journal *Geochimica et Cosmochimica Acta* in 1950 and of the *Geochemical Society* in 1955 marked the maturation of the field into a distinct scientific discipline.

3. The Scope of Geochemistry

Geochemistry consists of a number overlapping and interconnected subdisciplines. One broad distinction is between "low-temperature" and "high-temperature" geochemistry, although the dividing line between them is ill defined. Certainly, processes occurring from ambient surface temperatures to up to 100°C or so would fall within the range of low-temperature geochemistry while those at and above the temperatures of hydrothermal systems, 300–400°C, would fall within the realm of high temperature geochemistry. High- and low-temperature geochemistry can in turn be divided into a variety of subfields. Isotope geochemistry plays an important role in all of these. While geochemistry narrowly defined has an Earth focus, Earth is best understood, particularly its origins, in context of the Solar System of which it is part, and more broadly the universe in which its constituent elements have been created. These are the realms of cosmochemistry.

3.1. Low-Temperature Geochemistry.

Low-temperature geochemistry is focused on processes occurring at or near the surface of the solid Earth, including soil, the atmosphere, and oceans. It encompasses a wide range of topics including atmospheric chemistry, aquatic and groundwater chemistry, chemical oceanography, weathering, soil science, sedimentary chemistry, contaminant transport, biogeochemistry, and organic geochemistry including, but not limited to, formation and maturation of coal, petroleum, and natural gas. Environmental geochemistry is closely related but is focused on present processes. Space permits only a brief overview of a selection of these topics.

The Critical Zone. On land, a key focus is the "critical zone" (Figure 2), the region "extending from the outer limits of vegetation down to and including the zone of groundwater" (11). The term "critical zone" reflects the concentration of almost all terrestrial life within it, the dependence of humanity of on it, and the high sensitivity of it to anthropogenic disruption. Furthermore, chemical reactions within the critical zone also sustain life within the hydrosphere. Critical zone reactions are complex and involve many feedbacks and pathways and life is intimately involved in them.

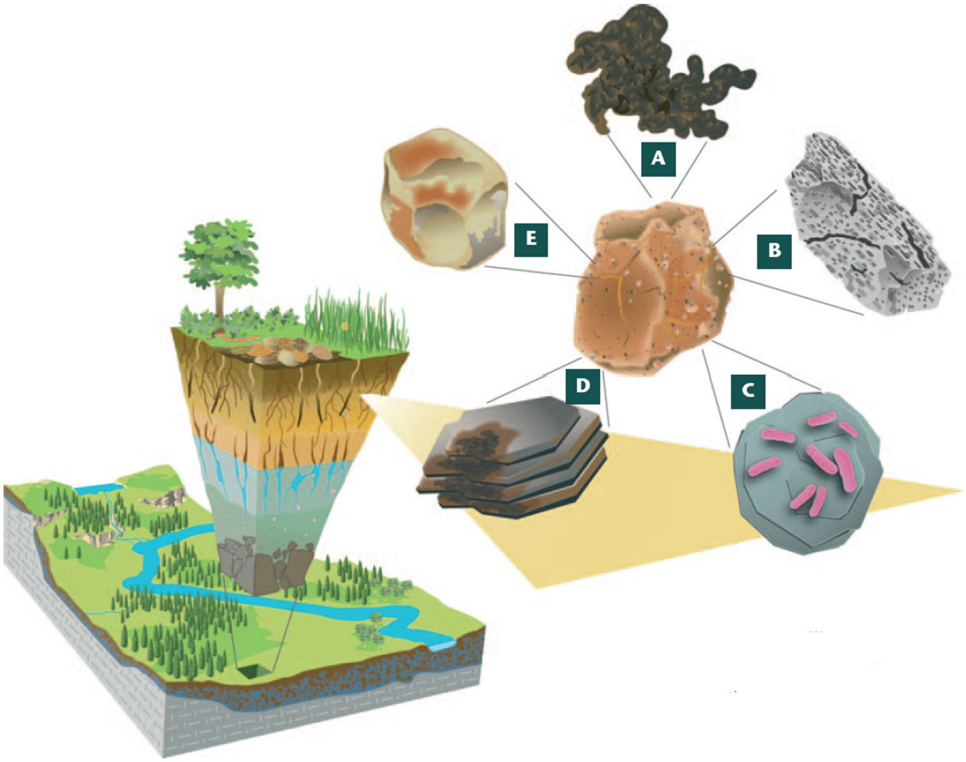

Fig. 2. The critical zone extends from the outer limits of vegetation down to and including the zone of groundwater. Almost all terrestrial life exist within this geochemically reactive region. Reactive surfaces within a typical soil aggregate (center, right) include of (A) natural organic matter, (B) nanoporous silicate minerals, (C) mineral–microbe complexes, (D) secondary aluminosilicate clays and their surface organic coatings, and (E) oxide and/or carbonate coatings. (Reprinted with permission from Ref. 11. Copyright 2006, Mineralogical Society of America.)

The key initial reaction is the weathering of crystalline rock, which can be represented by the following reactions:

$$2H_2O + CO_2 + 2NaAlSi_3O_8 \rightharpoonup Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+ + CO_3{}^{2-} \quad (1)$$

$$2H_2O + 2CO_2 + MgCaSi_2O_6 \rightharpoonup 4Si(OH)_{4(aq)} + Ca^{2+} + Mg^{2+} + 2CO_3{}^{2-} \quad (2)$$

$$2Fe_3O_4 + {}^1\!/_2O_2 + 3H_2O \rightharpoonup 6FeO(OH) \quad (3)$$

The left-hand sides of these reactions are typical igneous or metamorphic minerals, albite (feldspar), diopside (pyroxene), and magnetite, respectively. The right-hand side are weathering products: a dilute alkaline solution, dominated by alkali and alkaline earth cations and carbonate and bicarbonate anions (which approximates the composition of most rivers), plus soil minerals such as kaolinite, quartz, and goethite, respectively. The first of these reactions is an example of incongruent dissolution, that is, mineral breakdown in which only some of the components are released to solution, the second is an example of congruent dissolution, and the last is an oxidation/hydration reaction.

The minerals on the left can remain metastable indefinitely on dry planetary surfaces such as the Moon or Vesta but breakdown in the presence of water, hydrogen ions, and oxygen. The reactions above are simplifications of complex multistep reactions, the first of which is generally the attachment of a hydrogen ion to the mineral surface. Hydrogen ions in these examples are a consequence of the formation and dissociation of carbonic acid, with much of the CO_2 provided by respiration of soil organisms. Organic acids are an additional source of hydrogen ions and thus biological processes are a key part of the weathering process, although these would have been absent in the early Earth. From a biological perspective, the importance of these reactions is the release of plant nutrients, not only within the soil but also into streams, lakes, rivers, and oceans that receive the soil runoff, supporting biological productivity in those environments.

Current research on the critical zone involves learning about the kinetics of weathering reactions, including deducing exact reaction pathways and their dependence on factors such as temperature, rainfall, biota, rates of gas exchange, and anthropogenic disturbances (11). Chemical components are also cycled within the critical zone, between solution, soils, colloids, and the biota, so that the residence time of weathering products within it can be considerable (12). And although the example reactions above include only oxidation, complimentary reduction reactions also occur. This includes a continual cycling of nitrogen between N_2 and "fixed" nitrogen, which includes both oxidized and reduced forms such as NO_3^- and NH_4^-. This too is critical for life because, with the exception of some bacterial classes, autotrophs can only utilize fixed nitrogen.

Biogeochemistry and Biogeochemical Cycles. The focus of biogeochemistry ranges from microbial interactions with soil minerals in the critical zone to global biogeochemical cycles. The carbon cycle (Figure 3) is an example of such a cycle and one of key importance given the control that atmospheric CO_2 exerts on climate (5). Volcanoes introduce carbon in the form of CO_2 to the atmosphere. Its residence time in the atmosphere is short as it quickly cycles between the oceans, the biosphere, and soils. Geochemists define residence time as the amount of substance in a reservoir divided by the rate at which it is added or subtracted from it (the two are equal in the case of steady-state). At present, there are about 830 petagrams (pg) of carbon (as CO_2) in the atmosphere and the fluxes into the oceans (where it is converted to bicarbonate) and the biosphere (where it converted to organic carbon) are about 92 pg/yr and 112 pg, respectively (14), giving a residence time of about 4 years. In the absence of anthropogenic disturbance, roughly equal fluxes flow back into the atmosphere, but not always directly. Some carbon in the biosphere is stored in the soils, as leaf litter, peat, and other forms of soil carbon with a residence time of ~50 years. Of the reservoirs in this cycle, the atmosphere is the smallest, with roughly 600–1000 pg in the biosphere, 1200 pg in soil, peat, and permafrost, and 38,400 in the oceans (15). Some dissolved CO_2 in ocean surface water is fixed by phytoplankton and the remains of these organisms and those that graze on them then fall through the water column where organic carbon is converted back to dissolved CO_2 through respiration in the deep ocean. However, the vertical circulation of the oceans is quite slow, so that residence time of dissolved CO_2 in deep ocean water is on the order of 1000 years and the deep

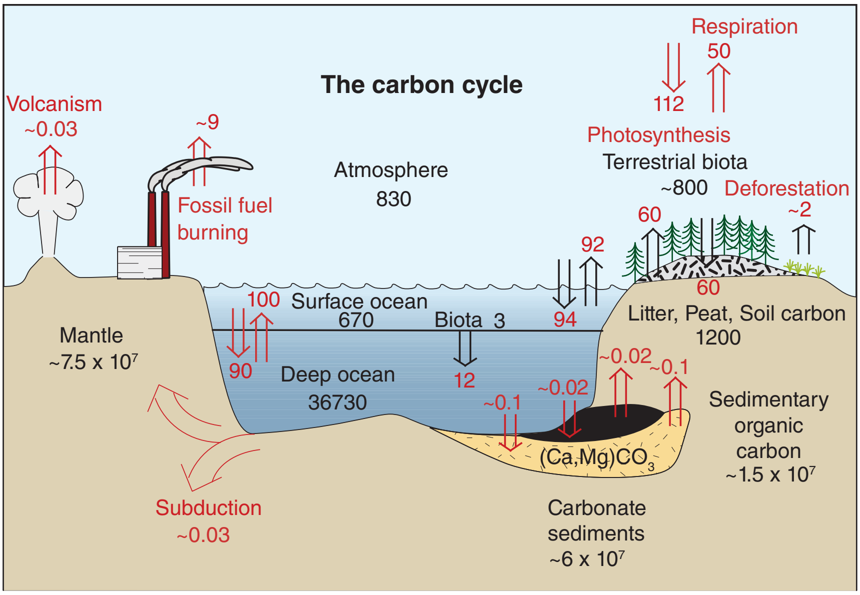

Fig. 3. The carbon cycle. Reservoir masses are in black italic type, fluxes between them are in red roman type. Units are 10^{15} grams. (Modified from Reference 10).

oceans contain nearly 50 times as much CO_2 as the atmosphere. This process whereby CO_2 is sequestered in the deep ocean is known as the biological pump. Changes in the efficiency of this pump and changes in ocean circulation during Pleistocene ice ages changed the ocean-atmosphere carbon balance, reducing atmospheric CO_2 concentrations from 280 parts per million by volume (ppmv) to 180 ppmv, greatly amplified the climate change induced by variations in Earth's orbit and rotation known as the Milkankovitch cycles (eg, 5).

The above could be described as the exogenic or short-term carbon cycle. A deeper cycle also operates, but at a much slower rate. Carbonate ions (including bicarbonate, which is generally more abundant) carried to the oceans by rivers are precipitated as calcium carbonate by a variety of marine organisms ranging from clams and corals to foraminifera and cocolithophores. Some of this calcium carbonate is buried as marine sediment. Additional carbonate precipitates within the oceanic crust and in pores between sedimentary particles (this is part of the process known as *diagenesis*: the conversion of sediments to sedimentary rock). Consequently, silicate weathering acts as a sink for atmospheric carbon dioxide. Variations in the rate of weathering have acted as one of the controls on atmospheric CO_2 and climate throughout the Phanerozoic (3). In addition, some of the organic matter produced by phytoplankton is not respired, but is buried along with marine sediment.

Vastly, more carbon is stored in sedimentary reservoirs than in all the exogenic reservoirs combined: approximately 6×10^{22} g as carbonate and 1.5×10^{22} g of sedimentary organic carbon (15). These are slowly returned to the exogenic cycle when sediments are exhumed and weathered and organic carbon oxidized to CO_2. In contrast, weathering of carbonates releases only carbonate ions, but metamorphic reactions in which carbonate minerals react with silicates do release CO_2, for example

$$CaCO_3 + SiO_2 \rightharpoonup CaSiO_3 + CO_2 \tag{4}$$

In addition, some carbonate in sediments and veins within the oceanic crust is subducted into the mantle where it also undergoes decarbonation reactions similar to (eq. 4), with the CO_2 released through volcanism, thus completing the cycle. The fluxes into and out of these reservoirs are quite small compared to fluxes between the exogenic reservoirs: approximately 0.1 and 0.02 pg/yr for the carbonate and sedimentary organic reservoirs, respectively.

Fluxes into and out of these long-term reservoirs are not always in balance, leading to changes in atmospheric composition. Fossil fuel burning since the industrial revolution has greatly accelerated loss from the sedimentary organic matter reservoir to approximately 9 pg/yr (16) and CO_2 has consequently increased from a preindustrial level of about 280 ppmv to a present (2016) level of ~400 ppmv. This increase, thus far at least, is small compared to variations in atmospheric CO_2 over Earth's history; those naturally driven changes, however, occurred far more slowly. Because it involves photosynthesis and respiration, the carbon cycle is closely linked to the oxygen and sulfur cycles, as well as to the behavior of redox-sensitive metals such as Fe, Mn, Mo, U, etc, and this has led to profound changes in the earth's chemistry.

There is considerable evidence that Earth's early atmosphere was quite different than the present one and was most likely dominated by CO_2 and N_2, similar to that of its sister planets, Venus and Mars (17,18). Photosynthesis, together with geologic burial of some fraction of the organic matter produced by that process, was responsible for the transition to the present N_2–O_2 composition (19). In addition to the geological and cosmochemical evidence, this is easily demonstrated by comparing the amount of buried sedimentary organic matter, roughly 1.7×10^{21} moles of carbon, with the amount of O_2 in the atmosphere, 3.75×10^{19} moles. Thus, oxygen in the atmosphere is a small fraction of that resulting from burial of organic carbon and some 1.6×10^{21} moles of oxygen have been consumed by other reactions, principally oxidation of iron and sulfur such as in reaction (3).

A variety of geochemical and geological approaches have now established that molecular oxygen became a significant atmospheric component only in the Paleoproterozoic about 2.3–2.4 billion years ago, a time known as the Great Oxidation Event, although some free oxygen may have been present earlier in ocean surface waters (20,21). While there is considerable consensus on the time of this event, there is debate as to when oxygenic photosynthesis first evolved. Although anoxygenic phototrophy very likely evolved in the Archean (2.5–4.0 billion years ago), direct evidence, including biomarkers, for early presence of oxygenic phototrophic organisms, cyanobacteria, has been challenged and is equivocal at best. Lyons and co-workers (22) nevertheless argued that the abundance of organic carbon in Archean shales requires oxygenic photosynthesis to have evolved hundred of millions of years before the Great Oxidation Event. That raises the question of why the delay? While there is no consensus, most theories center around a change in the nature of volcanism, as volcanic gases are reducing and thus work against photosynthesis (eg, 23,24). Other argue that oxygenic photosynthesis evolved only in the Paleoproterozoic and that oxygenation of the atmosphere followed very quickly (eg, 25).

Atmospheric oxygen levels remained low, however, perhaps little more than 1% of present levels, and deep ocean water remained anoxic until about 600–800 million years ago, when concentrations of redox sensitive elements in ancient marine sediments, such as Mo and U, indicate that oxygen levels began to rise toward present levels (22). It is probably no coincidence that multicellular animals, metazoans, first appear in the fossil record around this time (26).

Interestingly, this history of the evolution of free oxygen in the atmosphere is also closely linked to sedimentary iron formations, which are the world's principal source of iron ore, particularly the banded iron formations (BIFs). The earliest of these, formed 3.7 billion years ago, may have been produced by anoxygenic photosynthesis with Fe^{2+} serving as an electron acceptor. The largest, however, such as the Hamersley deposit in Australia and those around Lake Superior in North America, formed in the Late Archean and Early Proterozoic around the time of and shortly after (geologically speaking) the Great Oxidation Event. They likely formed as reduced deep ocean water rich in ferrous iron mixed with surface water oxygenated by photosynthesis, resulting in iron being oxidized to insoluble Fe^{3+} and precipitating (27).

Organic Geochemistry. As is clear from the preceding section, organic matter is an important part of the carbon cycle. Organic geochemistry is the study of organic matter outside of living cells in soil, water, air, and sediments. With rare exceptions, mostly restricted to simple hydrocarbons, this organic matter has been biologically produced.

Organic matter outside of cells is quickly attacked and broken down by bacteria and other organisms. This process releases nutrients, ie, converts them to inorganic form that can be utilized by autotrophs and, of course, produces CO_2. This results in far higher partial pressures of CO_2 in soils than in the atmosphere, contributing to weathering reactions 1 and 2, as well as higher dissolved CO_2 in ocean deep water; consequently, pH values in deep water are roughly ½ a pH unit lower than surface waters. Some biomolecules (defined here as molecules synthesized by organisms to directly support life), sugars, for example, are polar and readily soluble, while others, notably structural components of organisms, are nonpolar and hence hydrophobic and insoluble. Oxidation of these molecules by bacteria and other decomposers gives rise to the formation of oxygen-containing functional groups such as the hydroxyl and carboxyl group, which are polar, so that in the early stages of decomposition, the solubility of organic matter increases. Indeed, the amount of dissolved organic matter (DOC) significantly exceeds particulate inorganic matter (POC) in most natural waters, with the former ranging from 0.5 mg/l in open ocean water to 30 mg/l in bogs. Even rain and snow typically contain some DOC, although generally less than 1 mg/l.

Dissolved organic matter consists of relatively simple biomolecules and their breakdown products, including carboxylic and fatty acids, phenols, carbohydrates, amino acids, nucleic acids, etc, as well as more complex humic and fulvic acids formed by condensation from them. Many organic compounds, notably amino and carboxylic acids, readily complex transition metals such as Pb, Cu, Ni, Cd, Fe, etc, and humic and fulvic acids are rich in these functional groups. A substantial fraction of dissolved trace metals in natural waters may be complexed by these acids, enhancing their abundance as the solubility of these metals in natural aqueous solution is otherwise often quite limited (eg, 28).

Organic matter is also an important component of soils, typically constituting 6–10% by mass, but more in waterlogged soils. Soil organic matter plays an important role in soil fertility by releasing nutrients as it decomposes, stabilizing soil structure, increasing ion exchange capacity, and modulating porosity and water content. Recent advances in the past two decades have resulted in a paradigm shift as to the nature of soil organic matter and why it persists despite its thermodynamic instability (29,30). The long-held tradition view is that most soil organic matter consists of poorly structured, polymeric macromolecules known as humus, a term that includes insoluble humin as well as humic and fulvic acids. These form by condensation and polymerization of biomolecule fragments, and it was previously thought that their recalcitrant nature accounted for the persistence of organic matter in soils (31). Recent analytical and experimental advances suggest that humin may be the product of the extraction techniques traditionally used and instead much of soil organic matter may consist of molecular aggregates of partially decomposed plant polymers loosely held together by entropic interactions and/or noncovalent bonds and that such aggregates are not inherently stable against decomposition (29). Instead of molecular structure, environmental and biological factors, which remain poorly understood, appear to control the stability of soil organic matter (Figure 4) (30).

In the oceans and lakes, only a small fraction of the organic matter reaching the sediment–water interface is preserved, most is consumed by bacteria and other organisms living on or within the sediment, yet an enormous amount has been preserved over geologic time. Understanding how this organic matter is preserved

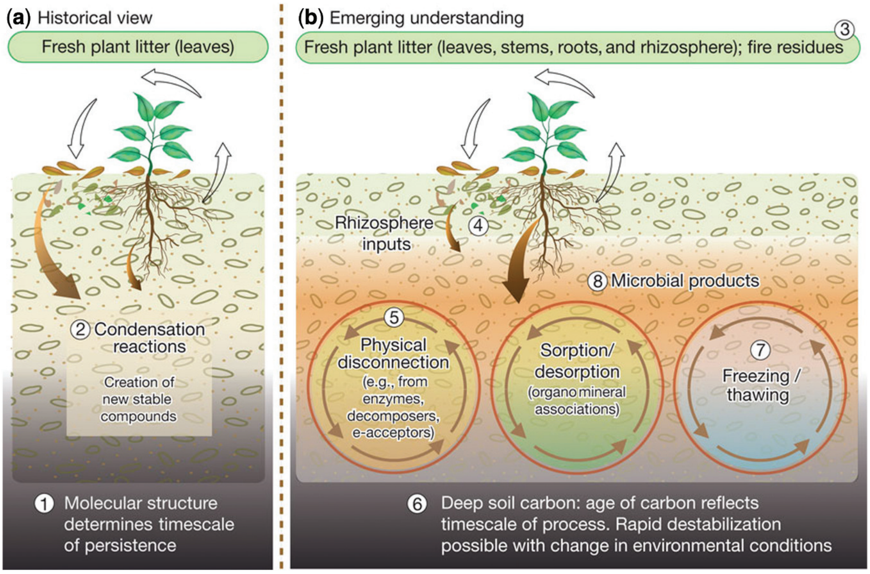

Fig. 4. Comparative views of the soil carbon cycle. (Reprinted with permission from Ref. 29. Copyright 2010, Nature Publishing Group.)

and how it is transformed is an important part of organic geochemistry, not the least because the small fraction ultimately transformed to petroleum, gas, and coal is such an important energy resource. The principal control on the preservation of organic matter in sediment is, not surprisingly, the difference between the rates of supply of organic matter and oxygen to sediments. High rates of productivity in surface waters result in high rates of accumulation of organic matter that, in turn, result in reducing conditions within the sediment, limiting the biota to anaerobic bacteria. Nevertheless, some organic matter survives even in aerobic environments, including some biomolecules or fragments of them that should be quite liable. Recent work suggests coprecipitation or chelation reactions result in macromolecular complexes between organic carbon and iron oxy-hydroxide minerals that stabilizes organic components (32) and explains their survival.

The organic matter that does survive in sediments is transformed by bacterial and chemical processes that are part of the diagenetic process. Functional groups such as carboxyl, amino, and hydroxyl are preferentially removed from their parent molecules resulting in decreasing oxygen, and to a lesser degree hydrogen, content of the organic matter. Unsaturated, aliphatic, and short-chained compounds decrease in abundance compared to saturated, aromatic, and long-chain ones. Hydrolysis of complex molecules produces a variety of molecular fragments that subsequently recombine with other molecules to produce new ones not present in the original biota. For example, phytol, produced by degradation of chlorophyll-a, and phenols, which can be produced by degradation of a variety of aromatic compounds, condense to form phenol–phytol compounds. In marine sediments, H_2S produced by sulfate-reducing bacteria is incorporated into carbon double bonds in long-chain compounds such as isoprenoids to produce thiol functional groups. The principal product of these processes is *kerogen*, the name given to the recalcitrant mixture of complex organic compounds that dominates the organic fraction in sediments.

As sediments are buried, they experience progressively increasing temperature and pressure and a number of new reactions begin as the organic matter attempts to come to equilibrium. These reactions are collectively called *catagenesis*. During this process, kerogen disproportionates into comparatively simple hydrogen-rich molecules (hydrocarbons) and a hydrogen-depleted carbon-rich residue. As temperatures in the range of 100–150°C are reached, the so-called "oil window," petroleum, a complex mixture of hydrocarbons, is produced. The petroleum is mobile and will migrate out of the source rock if a pathway exists. The first hydrocarbons to evolve in the oil window have on average relatively high molecular weight, $\sim C_{35}H_{54}$. This decreases to less than $C_{10}H_{18}$ at the peak of the oil window and continues to decrease at higher temperatures. As temperatures approach and exceed 150°C, natural gas, a mixture of methane with some short-chain hydrocarbons such as ethane and propane, is produced in the *metagenesis* stage. The degree of thermal maturation of kerogen is monitored from its H/C and O/C ratios. In the "oil window" the H/C ratio in the residual kerogen is less than 1 and the O/C ratio less than 0.1. kerogen with H/C ratios lower than 0.5 is over-mature, ie, it has already entered the metagenesis stage where methane is the principal hydrocarbon product.

Despite changes occurring during diagenesis and catagenesis, some organic compounds in petroleum retain some of the original chemical structure and can be

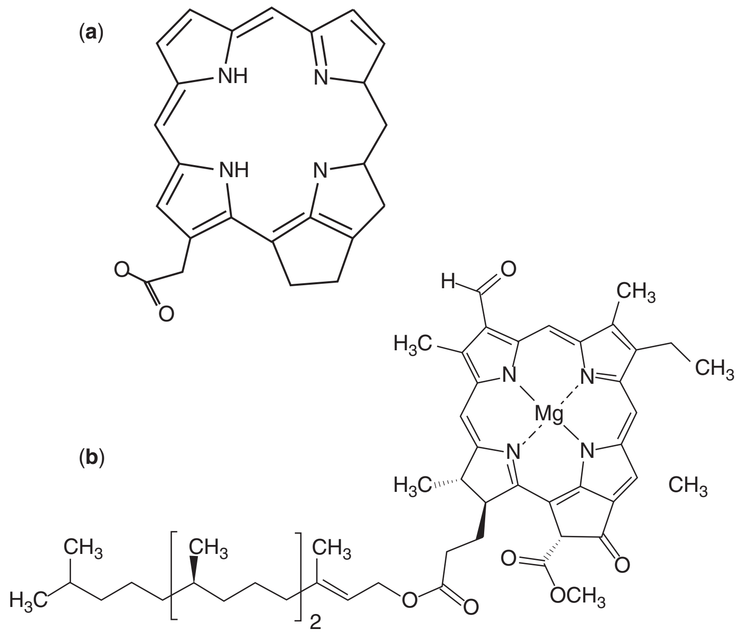

Fig. 5. Comparison of a porphyrin found in petroleum (**a**) and the chlorophyll molecule (**b**).

associated with specific classes of organisms. Indeed, the recognition by Treibs (33) that alkyl metalloporphyrins in petroleum were derived from chlorophyll (Figure 5) was the first clear demonstration of the biological origin of petroleum. Organic compounds such as these whose chemical structure can be related to compounds produced by specific classes of organisms are known as *biomarkers*. Biomarkers can be used to associate petroleum with the specific sedimentary source rocks and determine migration pathways (34). This in turn is useful in assessing the size and extent of deposits and identifying potential sites for further drilling. Biomarkers are also used to forensically associate hydrocarbon pollution with specific sources (eg, 35). They also have proved useful in unraveling the evolution of life (eg, 36). The carbon isotopic composition of C_{37} alkadienone, produced by marine haptophyte algae depends on the CO_2 concentration in surface water, which, in turn, reflects atmospheric CO_2 concentration. Carbon isotopic analysis of this compound has been used to determine atmospheric CO_2 over the last 40 million years, comprising much of the Cenozoic (37,38). Other organic compounds have proved useful for other paleoclimatology studies, including paleotemperatures (39).

Chemical Oceanography. The most fundamental observation about the chemistry of the oceans was made by Lavoisier, who, based on his analysis of seawater, wrote, "The water of the sea results from a washing of the entire surface of the globe; these are in some ways the rinsing of the grand laboratory of nature; one therefore expects to find mixed together in this water all the salts which can be encountered in the mineral kingdom, and that is indeed what is found." (40). In other words, the oceans are salty because rivers carry the products of rock weathering reactions into them and all chemical elements are present in seawater at some level. However, elements are not present in the oceans in the same proportion that they are present in the earth's crust. Incongruent weathering reactions such as equations 1 and 2 are one reason, but many other factors affect fluxes to the oceans such as reactions in estuaries (41). However, if rivers constantly carry salts to the sea, why, as Leonardo da Vinci wondered, have the oceans not become saltier over time?

Questions about processes that control seawater composition are an important focus of chemical oceanography. Seawater is a good example of an open, near steady-state system. Its composition is maintained by constant chemical fluxes into and out of seawater and the concentration of a given component in the oceans depends on the rate at which it is removed as well as the rate at which it is added. Excepting HCO_3, the major ions in seawater, Na, Ca, Mg, K, Cl, SO_4, are always present in constant proportions to one and other and to total salinity, as was postulated by Forchhammer (42) and demonstrated by Dittmar (43) based on analysis of samples collected during the HMS challenger expedition. These components all have very long residence times in seawater, hundreds of millions of years in some cases. Although the major element composition of seawater has been known since the nineteenth century, chemical oceanographers continue to improve understanding of the controls on it. For example, it was only through the discovery of deep-sea hydrothermal vents that it became clear that hydrothermal processes at mid-ocean ridges were the principal mechanism by which Mg is removed from seawater (44).

Although all the major ions in seawater are biologically utilized, the amounts present in seawater greatly exceed the amounts utilized by the biota. In contrast, both the residence times and the internal distribution of most trace components in seawater are controlled by biologic activity. Life utilizes a substantial fraction of the periodic table and many of these elements and their radicals are present only in low concentrations in seawater. Many nutrients and micronutrients are kept near zero concentrations in ocean surface waters through uptake by phytoplankton. Their organic remains are then remineralized as they sink through the water column. Consequently, the concentrations of bioutilized elements are higher in deep water than in surface water, often exhibiting a slight mid-depth maximum. Many nonbiologically utilized elements, such as Ge and Cd, show a similar pattern as they are inadvertently taken up by the biota in the course of assimilating chemically similar nutrients such as Si and Zn. Although the general outlines of these processes have been known for sometime, the oceans are so vast and sampling so limited, much of the detail is missing. Analytical advances and large-scale international sampling programs such as GEOTRACES in the last decade or two are greatly advancing knowledge of ocean chemistry, including chemical speciation of key nutrients such as Fe, and the distribution of anthropogenic contaminants such as Pb and Hg, and radioisotopes (eg, 45). As ocean water masses tend to have different concentrations, water chemistry can be used as tracers of water mass movement. Furthermore, incorporation of these tracers into sediments allows the reconstruction of past ocean circulation (eg, 46).

Geochemistry as History. Sediments are the history book of the planet's surface, recording everything from the evolution of life, oxygenation of the atmosphere, cataclysmic extinctions, motions of tectonic plates, erosion of ancient mountain belts, and climate changes to the origin of our own species and the rise of civilization. While much can be learned from sedimentary structures such as physical fossils, bedding planes, the minerals present and their shapes, sediment chemistry records even more. Some of these geochemical approaches to Earth history have already been mentioned in previous sections, including paleoclimate and paleoatmosphere proxies, but these are just a small sampling; a full accounting of these studies would require volumes. Many other of these paleoproxies are isotopic. Others are based on ratios of elements; for example, Sr/Ca ratios in some corals record variations in sea-surface temperatures (47).

Iridium is a highly siderophile element and consequently almost the earth's entire inventory is in its core and concentrations in the crust are extremely low. Thus, the discovery of a sharp peak in Ir concentrations (nonetheless reaching only a few parts per billion) in 65 million year-old sediments provided clear evidence of a major asteroid impact exactly at the end-Cretaceous extinction (48). Subsequent geochemical research has shown that massive eruptions of basalt at that same time in Deccan, India released CO_2 that produced climate warming and ocean acidification and may have had as much to do with the extinction as the impact (49). Understanding past climate change takes on new urgency to understand climate sensitivity to atmospheric chemistry as fossil fuel burning and deforestation are producing climate changes more rapidly than any known in the geologic past.

Geochemical approaches are increasingly used in archeological studies to document human and cultural history (50). Chemical and isotopic analysis of stone tools, ceramics, glass, marble, and metal have been used to document provenance of these materials and trace trade patterns (51–54). A recent example is the demonstration through trace element and isotopic analysis that fine-grained basalt adzes recovered from a rock shelter in Mangaia Island, Cook Archipelago were imported from as far away as Samoa and the Marquesas Islands, distances up to 2400 km and that this long-distance trade persisted from AD 1300 to ~AD 1600 (55). Strontium, oxygen, carbon, and nitrogen isotopes of human remains are routinely used to characterize the environment and diet of ancient peoples as well as their migrations (56,57), including human ancestors (58).

3.2. High-Temperature Geochemistry.

Igneous and Metamorphic Processes. High-temperature geochemistry focuses on magmatic, metamorphic, and hydrothermal processes occurring at temperatures well above those at Earth's surface. It is closely related to igneous and metamorphic petrology and mineralogy but expands these traditional topics by taking an approach based on chemical thermodynamics and kinetics and including trace elements and isotope ratios. Trace elements, despite their inconsequential abundances, have proved invaluable to these fields in part because their large variation in abundances, orders of magnitude, in similar rock types and because many elements are sensitive to factors to which major elements are insensitive, such as the extent of partial melting. Geochemistry also expands petrology's focus beyond the formation and evolution of rocks to the earth's formation and the subsequent evolution of the crust and mantle.

Melting of the earth and the volcanism that results from it have been central to Earth's evolution since it formed. Unlike its sister terrestrial planets, abundant volcanism persists today, although the pace has declined as Earth's temperature and heat production from radioactive decay have declined. Volcanism is entirely responsible for generating the earth's crust, of which there are two fundamental kinds, continental and oceanic. The latter is thin, dense, and ephemeral, nowhere older than a few hundred million years and generally far younger. It is continually destroyed and replaced by plate tectonic processes. In contrast, continental crust is thick, low density, and more or less permanent. The oldest known continental crust, in the Great Slave Craton of Canada, is 4 billion years old (59).

Why Earth melts to produce magmas and volcanoes was long a mystery, pondered by generations of geologists at least since James Hutton in the eighteenth century. The mystery was resolved in the second half of the twentieth century through a combination of a plate tectonic theory and thermodynamics. Tectonic plates move as a consequence of solid-state convection in Earth's mantle, which is how Earth loses its internal heat. This convection results in upwelling of hot mantle where plates diverge at mid-ocean ridges. Because of the relatively poor thermal conductivity of rock and the distance scales involved, this upwelling is effectively adiabatic and isentropic (until melt is lost). Thus, upwelling mantle will cool along an adiabatic temperature–pressure path as it rises, given by

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T\alpha V}{C_\mathrm{p}}, \tag{5}$$

where T is temperature, P is pressure, V is molar volume, α is the coefficient of thermal expansion, and C_p is the heat capacity, and the subscript S denotes an isentropic path. Multiphase solids such as rock melt over a range of temperatures: from the solidus where melting begins to the liquidus where it is complete. The slope of a phase boundary such as the solidus is given by the Clausius-Clapyeron equation

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_\mathrm{solidus} = \frac{\Delta V_\mathrm{melting}}{\Delta S_\mathrm{melting}}. \tag{6}$$

The slope of the solidus is steeper than the adiabatic gradient so, provided the mantle is initially hot enough, it will melt as it ascends, as is apparent in Figure 6. The mantle is never hot enough to cross the liquidus, so melting in the earth is essentially always partial (rare impact melts, including an extensive magma ocean formed following the Moon-forming impact, are an exception). Thus, volcanism at mid-ocean ridges is a consequence of decompression.

In the past 20 years or so, thermodynamic data and models have become complete enough to predict with useful accuracy not only the temperature and pressure when melting will occur but also the composition of melts produced, assuming the mantle composition is known (60). The task is nonetheless challenging. Mantle rock consists of eight or so major components whose abundance is great enough to influence the properties of the melt. As melting proceeds, the composition of the melt varies with temperature, pressure, volatile content, and melt fraction. To complicate matters further, the four or so solid phases that usually constitute the upper mantle are all solid solutions whose compositions that depend on these same factors. Routines such a pMELTS work by iteratively seeking the combination of liquid and solid solutions that yield the lowest Gibbs Free Energy of system at a given temperature and pressure. Once the magma rises to within 10 or

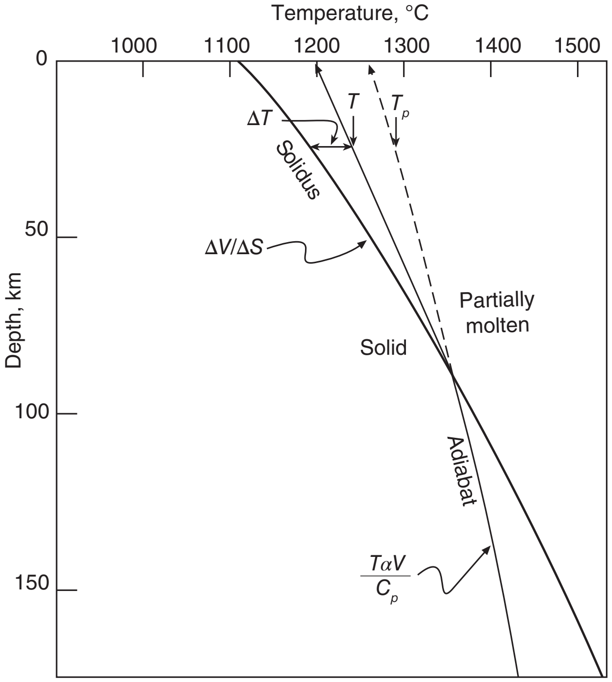

Fig. 6. Thermodyanmics of melting in a rising column of mantle rock. Below the solidus, the mantle rises along an adiabat. Once it intersects the solidus, some energy is consumed in melting to the *T*–*P* path becomes shallower. T_P is the potential temperature of the mantle before melting. (From Reference 13.)

20 km of the surface, it begins to cool and crystallize and its composition again evolves through fractional crystallization. The process, which is mainly responsible for the great chemical diversity of igneous rocks, can also be modeled with useful accuracy with these algorithms. Successful modeling requires accurately knowing the thermodynamic parameters of the phases as well as the interaction parameters of the major components. Those are measured in high-temperature, high-pressure experiments that were begun a century ago by Bowen (61). Uncertainty in these parameters continues to limit accuracy of these models, but progress continues to be made on refining them.

In contrast to volcanism at mid-ocean ridges, volcanism above subduction zones, such as the Northwest US, the Marianas, Indonesia, and the Andes, is perhaps better described as flux melting. Water lowers the solidus of silicate rock. As oceanic crust subducts beneath an overriding plate, hydrous minerals in the crust produced by reactions between the oceanic crust and seawater breakdown to form anhydrous ones. This water migrates into the overlying hotter mantle and induces melting. Magmas erupted above subduction zones are water-rich as a consequence and exsolution of this water as the magma decompresses accounts for the explosive, dangerous nature of these volcanoes. Water has a profound effect on the structure and thermodynamics of magmas and consequently water-rich magmas have proved more difficult to accurately model, but progress continues to be made. That should ultimately improve eruption forecasts.

Both the hydration of the oceanic crust in hydrothermal systems and its dehydration in subduction zones are examples of metamorphic reactions. Here again, a thermodynamic approach has proved useful. Most mineral phases in metamorphic systems are also solid solutions and their compositions depend on the temperature, pressure, and composition of the system. While this certainly imposes a burden on the kind of modeling described above, it also provides an extremely useful tool, it is possible to calculate the temperature and pressure at which a mineral assemblage equilibrated if their compositions and thermodynamic properties are accurately known (eg, 62,63). Typically, two pairs of minerals are generally needed to constrain both temperature and pressure. Mineral-pair reactions that have a large volume change (ΔV) and low enthalpy change (ΔH) of reaction are most dependent on pressure and therefore serve as geobarometers. Conversely, reactions with small ΔV and large ΔH serve as good geothermometers. The combination of Ti in quartz and Zr in rutile (TiO_2) is an example of a pair of reactions from which T and P can simultaneously be determined (64). Knowing the temperature and pressure at which metamorphic rocks formed is enormously useful in reconstructing geologic history. Thermobarometers are also widely used in igneous petrology. One caveat is the usual one in thermodynamics, namely, that thermobarometry assumes equilibrium between phases. Kinetic factors may impede equilibrium, so that understanding the kinetics of metamorphic reactions is also important.

Hydrothermal Systems, Ore Deposits, and Mine Wastes. Ore deposits are geochemical accidents, particularly for rare elements. They result from scavenging those elements from large volumes of rock and concentrating them in small volumes, sometimes at concentrations orders of magnitude above their crustal abundances. The practical importance of volcanism and metamorphism is (other than having created the land we walk on) that many, and perhaps most, of the ores of metals upon which civilization depends form as a consequence of volcanism or metamorphism. There are exceptions, of course, where sedimentary or weathering processes are responsible for ores, for example, the banded iron formations discussed previously, bauxite, the principal ore of Al, which forms from highly weathered soils and Li from brines, but most ore bodies form at depth at elevated temperature. Some metals, notably the platinum group metals, Ti, Cr, Co, and Ni can be concentrated to ore grade by purely magmatic processes when minerals rich in these metals precipitate in restricted zones from magma chambers or in magmas, such as carbonatites, that are enriched in elements such as the Nb, U, and the rare earths. More often, ores precipitate from heated aqueous fluids with magmatism or metamorphism providing both the heat and the thermal gradients to drive fluid convection. The water, however, may be deeply circulating meteoritic groundwater or water that exsolved from magma.

In the past, many ore deposits were found simply by stumbling over them, such as the Río Tinto mine, discussed below, which has been mined since prehistory. Today, all readily apparent deposits exposed as the surface have long since been found and many, as is the case in Río Tinto, have been mined out. Understanding how ores form and recognizing clues on the surface to the existence of ores at depth has thus become critically important to filling society's continuing demand. Furthermore, modern technology requires copious supplies of some metals, such as Te, Li, and the rare earths, that were little used in the past.

Space does not permit discussion of the hydrothermal chemistry of the entire periodic table, but gold geochemistry can serve as an example; more detailed information on ore deposits can be found in *Treatise on Geochemistry* (65).

Gold is one of the oldest metals humans learned to extract and work. Its principal value was in ornamentation as a display of wealth and power. Today it is used more often as a store of wealth, but also finds broad use in other applications such as electronics. Much of its value lies in its inertness, raising the question of just what chemical processes could extract, transport, and ultimately concentrate this element whose crustal abundance is roughly 1 part per billion to "economic" levels of at least 1 part per million and sometimes 10's or 100's of ppm. Scientists have pondered this question at least since Agricola (66), who seems to have understood that gold was carried and deposited into veins by heated groundwater.

Since the first hydrothermal gold experiments by Ogryzlo (67), geochemists have made considerable progress in understanding how gold is transported in aqueous solutions using techniques ranging from experimental (68) to *ab initio* molecular dynamics (69). In hydrothermal solutions a number of ligands form stable gold complexes, including HS^-, $S_2O_3^{2-}$, CN^-, SCN^-, and chloride and polychloride species (70). Which dominates depends on temperature, pressure, redox state, and solution composition (eg, 71). Some aspects of this complexity are illustrated in Figure 7. Gold is leached from its source, which is often subduction-related igneous rocks (72,73), under conditions of high-gold solubility. Relatively

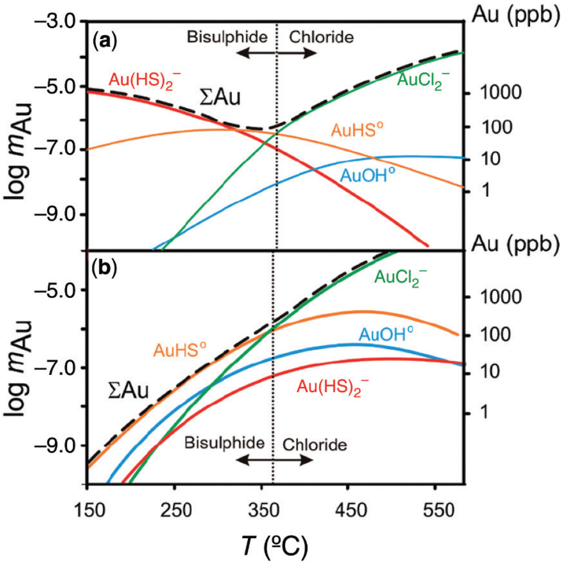

Fig. 7. Gold speciation in sulfide- and chlorite-bearing hydrothemal solutions containing 1.5 molal (m) NaCl and 0.5 m KCl, with pH buffered by the assemblage K-feldspar–muscovite–quartz at 100 MPa. (**a**) ΣS (total S) = 0.01 m and fO_2 (oxygen fugacity) is buffered by the assemblage hematite–magnetite. (**b**) ΣS and fO_2 are buffered by pyrite–pyrrhotite–magnetite; the maximum value of ΣS is 0.1 m. The black dashed line (ΣAu) indicates the total solubility of gold. (Reprinted with permission from Ref. 63. Copyright 2011, Mineralogical Society of America.)

small changes in fluid composition, temperature, or pressure subsequently result in a rapid drop in solubility and precipitation of gold, forming the ore. In the last two decades, geochemists have also realized that gold can be transported in colloidal form associated with colloidal silica (74,75). Sudden coagulation and precipitation of these colloids can then occur when conditions change, explaining the common association of gold with quartz veins.

Beyond understanding how ore deposits form, geochemistry also plays an increasingly important role in finding them. Most ore deposits exposed at the surface have been found; those that remain are buried beneath the regolith. Elements concentrated in ore deposits represent a low entropy situation and they inevitably tend to disperse into the surrounding environment. Consequently, there is often a subtle geochemical signature on the surface of ore deposits at depth and the minerals industry is increasing relying on geochemistry to identify new exploration targets and to delineate the extent of known deposits and thus inform mine expansion (76,77). These subtle signatures may be elevated concentrations of the metal of interest, but may also be elevated concentrations of other, rapidly diffusing elements such as the halogens or enrichments of other metals in specific minerals. An example of the latter is the enrichment of W in rutile (TiO_2) as a pathfinder element for gold (76).

While mining and refining metals has been key to the development of civilization, it also has and continues to impose a burden on society. Typically, 95–99% of rock removed in mining operations is waste and in the case of low-grade gold ores that fraction can be even higher. The amount of mine waste generated annually vastly exceeds commercial and household wastes and is comparable to the amount of solids moved by natural geologic processes (78). While this in itself can blight the landscape, the bigger problem is that this material is often toxic. The problem is particularly acute when the ores consists partly or wholly of sulfide minerals, which is often the case, particularly for so-called “base metal” ores such as Cu, Pb, and Zn. When exposed to oxygenated water, sulfides quickly undergo oxic weathering, for example, pyrite will react to form ferrihydroxide and sulfuric acid. The overall reaction may be written as follows:

$$\mathrm{FeS_2} + \frac{15}{4}\mathrm{O_2} + \frac{7}{2}\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_3} + 2\mathrm{H_2SO_4} \tag{7}$$

In actuality, the oxidation is often carried out by iron-oxidizing bacteria, as the kinetics of the biologically mediated reaction are much faster than the abiologic one at low pH.

The consequences of this is what is known as *acid mine drainage* and is illustrated by the Río Tinto (dyed river) in Andalusia in southern Spain. This river drains the mine from which the giant international mining conglomerate Rio Tinto gets it name. The deposit is classed as a volcanogenic massive sulfide originally formed by a submarine hydrothermal system. Some 5000 years of mining of copper, silver, gold, and other metals as well as natural weathering have given the river a reddish hue (Figure 8) due to the presence of dissolved iron and the banks are lined with effervescent sulfate minerals. pH values of 2 and less extend

Fig. 8. The Río Tinto in southern Spain is discolored by the weathering products of sulfides, both those naturally occurring at the surface and those exposed by millennia of mining operations. Photo by Carol Stoker, NASA Ames Research Center.

60 km downstream from the mine nearly to the estuary and tidal flat. Toxic levels of Cu, Zn, As, and Pb are found in sediments along the entire length of the river (79). This chemistry makes the river nearly barren of life except for extremophile microbes and a few rare and unusual eukaryotes.

Preventing future environmental problems and mitigating past ones requires understanding how elements in mine waste behave in the near-surface environment. Thus, for example, sulfide-rich tailings should be disposed of in a way that maintains a reducing environment to prevent oxidative dissolution as in equation 7. In contrast, in ores that have been processed by roasting, highly toxic elements such as As and Sb are hosted in oxide phases and are rather immobile in that state. Consequently, future remediation of those sites should insure that they do not become reducing, in which case such minerals may undergo reductive dissolution, releasing As and Sb to solution (80).

3.3. Isotope Geochemistry. The isotopic makeup of elements can vary due to either nuclear or chemical processes. Radioactive decay is the most important such nuclear process by a wide margin, but cosmic ray spallation also produces isotopic changes in the atmosphere and Earth's surface and far more rarely, neutrons and α-particles can induce secondary nuclear reactions. Radiogenic isotope geochemistry is the study of isotopic variations resulting these nuclear processes. While neutrons play no direct role in chemical processes, the mass difference resulting from the presence of extra neutrons in an atom do have a secondary effect on bond strength and diffusivity. As a consequence, chemical processes can change, or fractionate, the isotopic composition of elements. Stable isotope geochemistry is the study of these changes.

Radiogenic Isotope Geochemistry. Radioactive elements, principally U, Th, and K, are important because their decay within the earth supplies a significant fraction, between a third and half, of the energy to drive mantle convention and consequently plate tectonics and associated geologic processes (the remainder of the energy is initial heat left over from Earth's formation). Radioactive decay can be expressed as a simple first-order rate equation

$$\mathrm{d}N/dt = -\lambda N, \tag{8}$$

where N is the number of atoms of a radioactive isotope, t is time, and λ is the decay constant. The great value of radioactive decay to the earth scientists is that this rate constant is independent of all environmental influences and thus decay precedes at an absolutely constant rate (caveat: a slight dependence on the rate of electron capture decay of ^{40}K to ^{40}Ar on pressure has been found and at temperatures well beyond those found in the earth, and nuclei can be excited into higher energy states from which they decay at different rates). Thus, decay produces daughter nuclides at a constant and predictable rate. Rearranging and integrating, the number of radiogenic daughter nuclides D^*, produced over time t, is

$$D^* = N(\mathrm{e}^{\lambda t} - 1). \tag{9}$$

This equation and ones derived from it form the basis of measuring geologic time. Yale chemist Bertram Boltwood was the first to recognize this potential and in 1908 he reported ages of U-rich minerals based on the amount of Pb in them of up to 2.2 billion years (81). This implied that Earth and Sun were vastly older than the 20 million years that Lord Kelvin had estimated assuming the Sun's energy was derived from gravitational contraction. Boltwood's ages were somewhat incorrect, however, because he did not realize that two isotopes of U, ^{238}U and ^{235}U decayed to ^{206}Pb and ^{207}Pb, respectively, at different rates. Once this was taken into account, Alfred Nier was able to make more accurate measurements, but found similarly old ages (82). Subsequent geochronology over the last century has enabled geochemists to firmly establish the age of Earth at 4.5 billion years (83) and to put absolute ages on the relative geologic time scale that geologists had assembled more than a century earlier based on the appearance and disappearance of fossil biota. Thus, for example, the boundary between the Mesozoic Era/Cretaceous Period and the Cenozoic Era/Paleogene Period, the K/Pg boundary (formerly known as the Cretaceous-Tertiary or *K–T* boundary) is precisely dated at 66.043 million years before present with an uncertainty of only 11,000 years (84). Until recently, radiometric dating has required samples in-hand for laboratory analysis, limiting its application to terrestrial samples and meteorites, but in 2014 NASA's Curiosity rover carried out the first successful extra-terrestrial age measurement on Mars, determining a K–Ar age of 4.21 ± 0.35 billion years for the mudstone on the floor of Gale Crater (85).

Isotopes of nine elements whose half-lives are long enough that they survive in measurable abundance on Earth, yet short enough that they produce measurable isotopic variations in their radiogenic daughter elements are the basis of radiogenic isotope geochemistry (Figure 9). These half-lives range from 7×10^8 years for ^{235}U to 4.5×10^{11} years for ^{190}Pt (Table 1). Variations in the abundances of radiogenic isotopes produced by decay of shorter-lived nuclides that are now "extinct," such as ^{26}Al, ^{53}Mn, ^{129}I, ^{146}Sm, ^{182}Hf, and ^{244}Pu, have been studied in meteorites and, in a few cases, terrestrial rocks. Cosmogenically

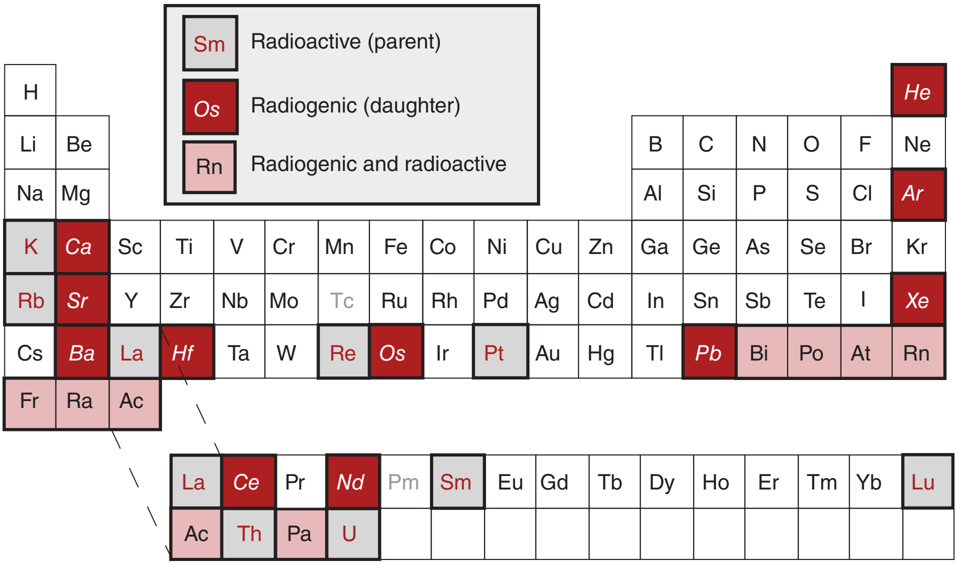

Fig. 9. Radioactive and radiogenic elements used in isotope geochemistry. (From Reference 80.)

produced radionuclides, such as ^{14}C, ^{10}Be, ^{36}Cl, etc, also decay at constant rate and are also used in geochronology. These generally have short half-lives and are mostly useful in archeology and recent geological history. Accurate dating using these chronometers requires the additional step of taking account of production

Table 1. **Geolochemically Useful Radioactive Decay Schemes**

Parent	Decay Mode	λ (yr^{-1})	Half-life (yr)	Daughter	Ratio
Cosmogenic Radionuclides					
^{14}C	β^-	1.209×10^{-4}	5730	^{14}N	
^{10}Be	β^-	4.62×10^{-7}	1.500×10^{6}	^{10}B	
^{36}Cl	β^-, $\varepsilon\cdot\chi$, β^+	2.25×10^{-6}	3.08×10^{5}	^{36}S, ^{36}Ar	
Long-Lived Radionuclides					
^{40}K	β^-, $\varepsilon\cdot\chi$, β^+	5.549×10^{-10}	1.28×10^{9}	^{40}Ar, ^{40}Ca	^{40}Ar/^{36}Ar
^{87}Rb	β^-	1.42×10^{-11}	48.8×10^{9}	^{87}Sr	^{87}Sr/^{86}Sr
^{138}La	β^-, β^+	2.67×10^{-12}	2.59×10^{11}	^{138}Ce, ^{138}Ba	^{138}Ce/^{142}Ce
^{147}Sm	α	6.54×10^{-12}	1.06×10^{11}	^{143}Nd	^{143}Nd/^{144}Nd
^{176}Lu	β^-	1.87×10^{-11}	3.6×10^{10}	^{176}Hf	^{176}Hf/^{177}Hf
^{187}Re	β^-	1.64×10^{-11}	4.23×10^{10}	^{187}Os	^{187}Os/^{188}Os
^{190}Pt	α	1.54×10^{-12}	4.50×10^{11}	^{186}Os	^{186}Os/^{188}Os
^{232}Th	α	4.948×10^{-11}	1.4×10^{10}	^{208}Pb, ^{4}He	^{208}Pb/^{204}Pb
^{235}U	α	9.8571×10^{-10}	7.07×10^{8}	^{207}Pb, ^{4}He	^{207}Pb/^{204}Pb
^{238}U	α	1.55125×10^{-10}	4.47×10^{9}	^{206}Pb, ^{4}He	^{206}Pb/^{204}Pb
Extinct Radionuclides					
^{26}Al	β^-	9.68×10^{-7}	7.16×10^{5}	^{26}Mg	^{26}Mg/^{24}Mg
^{53}Mn	β^-	1.87×10^{-7}	3.7×10^{6}	^{53}Cr	^{53}Cr/^{52}Cr
^{107}Pd	β^-	7.37×10^{-8}	9.4×10^{6}	^{107}Ag	^{107}Ag/^{109}Ag
^{129}I	β^-	4.41×10^{-8}	15.7×10^{6}	^{129}Xe	^{129}Xe/^{130}Xe
^{146}Sm	α	1.02×10^{-8}	$68 \pm 7 \times 10^{6}$	^{142}Nd	^{142}Nd/^{144}Nd
^{182}Hf	β^-	7.79×10^{-8}	8.9×10^{6}	^{182}W	^{182}W/^{184}W
^{244}Pu	fission	8.45×10^{-9}	82×10^{6}	$^{131-136}$Xe	^{136}Xe/^{130}Xe

rates that vary somewhat due to astrophysical and other factors. This usually involves calibration, for example, against conventional radiometric chronometers or tree rings.

Geochronology requires the rocks and minerals investigated to have been closed systems, ie, no loss or gain of either radiogenic daughter or radioactive parent; violation of this requirement is a major source of error in geochronology, usually resulting in ages that are too young. This condition can be evaluated in a number of ways and in some approaches, for example, dating of U-rich minerals such as zircon or the step-heating $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ technique widely used for the $^{40}\mathrm{K}$-$^{40}\mathrm{Ar}$ system, age information can be recovered even where the system has not been completely closed (86).

However, radiogenic isotopes have value far beyond geochronology. In most cases geochemists work with isotope ratios rather than just abundances. Using the example of $^{143}\mathrm{Nd}$ produced by α-decay of $^{147}\mathrm{Sm}$, the dependence of a radiogenic isotope ratio on time can be expressed as follows:

$$\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}} = \left(\frac{^{143}\mathrm{Nd}}{^{144}\mathrm{Nd}}\right)_0 + \frac{^{147}\mathrm{Sm}}{^{144}\mathrm{Nd}}(e^{\lambda t} - 1), \tag{10}$$

where $(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_0$ is the ratio at the initial time, ie, $t = 0$. Thus, how the $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio increases with time depends on the Sm/Nd ratio in the reservoir in which that Nd resides. Chemical differentiation of the earth has produced reservoirs with different Sm/Nd ratios and hence different $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratios. For example, when new continental crust is created by magmatism, the Sm/Nd ratio of that crust will be lower than that of the mantle from which it is derived, because Nd is enriched relative to Sm in the melts forming the crust. The longer Nd resides in the crust, the more its $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ growth will lag that of the mantle. Hence, old crust has lower $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ than young crust.

These differences can be used effectively as tracers both at the surface of Earth and in its interior. $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ in seawater provides an example of the former. Because rivers draining old crust supply water and salts in the Atlantic Ocean, whereas the Pacific is surrounded by relatively young crust, Pacific Ocean water has higher $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ than Atlantic water. Neodymium in water masses is sampled by manganese nodules growing slowly on the ocean floor. Consequently, analysis of Nd isotope ratios as a function of depth in these nodules can be used to compare modern and ancient ocean circulation patterns (87).

Another example illustrates the power of isotope ratios as tracers in the earth's interior. Subduction of oceanic crust is an important part of the plate tectonic cycle and, as was described earlier, volcanism above subduction zones is triggered by water released from that crust as it subducts. Armstrong (88) recognized very early that Pb isotope ratios in these volcanic rocks carried the signature of marine sediments and argued that sediments were subducted along with the underlying basaltic crust. The importance of this was that continental crust was not necessarily completely permanent as had been thought, but could be eroded, subducted, returned to the mantle (89), and eventually returned to the surface through mantle plumes (90). That idea was controversial until Tera and co-workers (91) demonstrated the presence of $^{10}\mathrm{Be}$, albeit minute amounts, in subducted-related lavas while demonstrating its absence in all other lavas. Since

^{10}Be has a half-life of only 1.6 million years and is created only by cosmic-ray spallation in the atmosphere, they concluded the ^{10}Be must be derived from subducted sediments.

Stable Isotope Geochemistry. In 1947, Urey (92) and his University of Chicago colleagues Bigeleisen and Meyer (93) demonstrated theoretically that neutron mass has an effect on chemical bonding and that this effect depends on temperature. These papers mark the birth of stable isotope geochemistry. In addition to this effect on the equilibrium distribution of isotopes among phases, nuclear mass also affects diffusion and reaction rates, and the ability of molecules to transition between energy states, which leads to kinetic isotope fractionations. These effects are quite small and typically lead to a percent or less variation in the isotopes ratios, although variations in the ^{2}H/^{1}H ratio can be tens of percent. Traditionally, the focus of this field has been on a handful of light elements, H, C, N, O, and S, that are abundant, have large relative mass differences between isotopes, participate in a wide variety of bonds, and/or occur in multiple valence states. Consequently, isotopic variations in these elements tend to be large and are readily measured. In the past several decades, stable isotope geochemistry has expanded to include a wide variety of multi-isotopic elements, including the heaviest, U (94). Stable isotope ratios are generally reported in δ-notation, which is the per mil deviation of the ratio in sample from that in a standard, for example, hydrogen isotope ratios are reported as follows:

$$\delta D = \left(\frac{\left(\frac{^{2}\mathrm{H}}{^{1}\mathrm{H}}\right)_{\mathrm{sample}} - \left(\frac{^{2}\mathrm{H}}{^{1}\mathrm{H}}\right)_{\mathrm{SMOW}}}{\left(\frac{^{2}\mathrm{H}}{^{1}\mathrm{H}}\right)_{\mathrm{SMOW}}} \right) \times 1000, \qquad (11)$$

where SMOW, or standard mean ocean water (also sometimes denoted as V-SMOW, referring to the standard distributed by the International Atomic Energy Commission in Vienna), is the universally agreed upon standard.

Urey quickly realized that the temperature dependence of isotopic fractionation provided the potential for determining paleotemperatures. His students and postdocs demonstrated in laboratory experiments that actual fractionations reasonably matched the predicted ones. He then set his student Casare Emiliani to the task of determining O isotope ratios in the calcite shells of planktonic foraminifera from deep-sea cores with the goal of unraveling the temperature history of Pleistocene Ice Ages. From his work, Emiiani concluded that these climate swings were a consequence of small variations in Earth's orbit and rotation, as Milutin Milanković had theorized half a century earlier (95). Compared to subsequent studies, Emiliani's work was rather primitive and not all his conclusions have held up. However, the idea that Milankovich cycles were the primary driver of climate cycles in the Pleistocene and earlier geologic epochs has become a central paradigm in paleoclimatology and established stable isotope ratios as the premier paleotemperature proxy. In subsequent decades, oxygen has been augmented by studies of hydrogen isotopes in Antarctic and Greenland ice sheets, providing an extraordinarily detailed history of Pleistocene climate oscillations (eg, 96,97).

Photosynthesis is the principal cause of variations in carbon isotope ratios and all biogenic organic compounds are depleted in ^{13}C, typically in the range of 15–25 or more per mil. These isotopic fractionations result from a combination of more rapid diffusion of into cells and the slightly weaker bonds and hence higher reactivity of $^{12}CO_2$ compared to $^{13}CO_2$ and are universal in all autotrophic organisms, including chemosynthetic ones, although the extent of fractionation varies somewhat between classes of organisms. That petroleum carries this isotopic signature removes any doubt of its ultimate biological origin. That same signature is found in a subset of diamonds carrying eclogitic inclusions, leading to the much more surprising inference that the carbon in them was derived from organic matter carried at least 100 km into the mantle (98). This ^{13}C-depleted signature is also found in graphite inclusions in apatite crystals in 3.8 billion year-old metasediments from Isua, Greenland and has been interpreted as evidence of life at that time (99). This interpretation remains controversial, but the recent discovery in the same area of 3.7 billion year-old stromatolites (100), the modern examples of which are structures created by bacteria, greatly strengthens the case for the early appearance of life on Earth.

While photosynthetically produced compounds are depleted in ^{13}C, the remaining inorganic carbon in a reservoir such as the ocean is necessarily enriched in ^{13}C. This has been exploited to trace both ocean circulation and the intensity of biologic productivity through time (101), demonstrating, among other things, that the great mass extinctions such as the end-Cretaceous event did not merely reduce biological diversity, but catastrophically reduced biological productivity as well (102).

Isotope fractionation results mainly from the effect of mass on the translational, vibrational, and rotational motion of atoms and molecules, but it is the effect on vibrational motion that is dominant and principally responsible for the temperature dependence of fractionation. The fractionation between two phases A and B is generally quantified as the fractionation following factor:

$$\alpha_{\mathrm{A-B}} = \frac{R^{i,j}_{\mathrm{A}}}{R^{i,j}_{\mathrm{B}}}, \tag{12}$$

where $R^{i,j}$ is the ratio of isotopes i and j. Because the fractionation is generally small and ratios are usually reported in δ-notation, the fractionation factor can also be defined as

$$\Delta_{\mathrm{A-B}} = \delta_{\mathrm{A}} - \delta_{\mathrm{B}} \cong 10^3 \alpha_{\mathrm{A-B}}. \tag{13}$$

For simple diatomic molecules, calculation of equilibrium fractionations is straightforward from quantum mechanics when vibrational frequencies are known (eg, 93), but rapidly become complex in multiatomic molecules and crystals where many vibrational modes are possible. Consequently, equilibrium fractionation factors have historically been determined experimentally. In the last decade or two as greater computation power has become available, it has become possible to calculate fractionation factors and their temperature dependencies from first principles (eg, 103,104).

Fractionation factors decrease approximately with the inverse square of temperature and they are generally quite small at magmatic and mantle temperatures ($\gtrsim$1000°C). Nevertheless, the temperature dependencies of isotope fractionation have proved useful as geothermometers in a wide variety of situations beyond the ocean and ice temperature records mentioned previously. This includes, among other applications, determining the temperatures of sulfide ore deposition from the sulfur isotope composition of coexisting sulfide phases, although this assumes equilibrium between phases, which is not always achieved (eg, 105). Even when not useful as geothermometers sulfur isotope ratios can be useful in identifying the source of ore forming fluids (eg, 106).

Most isotopic fractionation is mass dependent, which is to say the extent depends of the mass difference between the two isotopes of interest. Thus, for example, the fractionation between ^{17}O and ^{16}O is roughly half of that between ^{18}O and ^{16}O. Mass-independent fractionation, where this is not the case, was first identified in oxygen in meteorites (107) and is thought to have resulted from photolysis of CO in the solar nebula by UV light emitted by the growing Sun. The mechanism appears to involve "self-shielding," where the wavelengths necessary to dissociate the abundant species C^{16}O (^{16}O is >99% of all O) is completely absorbed close to the Sun while wavelengths necessary to dissociate C^{17}O and C^{18}O are able to penetrate much further from the source (108).

Mass independent fractionation has also been identified in sulfur isotopes of sulfides and sulfate from sediments older than about 2.3 billion years (20). The cause again seems to have been UV photolysis and self-shielding, in this case of atmospheric SO_2. This does not occur to a significant degree in the modern atmosphere, because most UV light is absorbed by O_2 and O_3 in the stratosphere and, additionally, the chain of chemical reactions involved appears to require very low oxygen abundance (109). The cessation of mass independent fractionation of sulfur isotopes coincides in time with the Great Oxidation Event 2.3 billion years ago inferred from other geochemical indicators and confirms that the atmosphere first became oxidizing at this time.

Surprisingly, this Archean mass-independent sulfur isotope fractionation has been detected not only in diamonds from depths of 100 km or more (110) but also in sulfide in lavas from the islands of Mangaia, Cook Archipelago (111), and Pitcairn, Gambier Archipelago (112), both in the central Pacific Ocean. Oceanic islands such as these are produced by upwelling columns of hot mantle, known as mantle plumes, which can be traced seismically to the base of the mantle (113). This, and other trace element and isotopic evidence demonstrates that material from the earth's surface can be subducted into the deep mantle and ultimately returned again to the surface (114), a geochemical cycle encompassing the entire outer half of the planet.

The noble gases isotopes are of particular interest in isotope geochemistry because many are produced either by radioactive decay, secondary nuclear reactions triggered by radioactive decay, cosmic rays, or have experienced mass-dependent fractionation (eg, 115,116). Noble gas isotope geochemistry has been applied to studies as diverse as fluids, including both groundwater and hydrocarbons, in the crust, ocean circulation, and erosion rates. Xenon isotopes produced by decay of the extinct radionuclides ^{129}I and ^{244}Pu provide clues to Earth's earliest history and the origin of its atmosphere (117).

3.4. Cosmochemistry. Earth's formation is intimately linked to the formation of the Sun, its sister planets, and other objects in the Solar System. However, among these objects Earth is uniquely habitable. That habitability is in large measure a consequence of events occurring as the Solar System formed – producing a rocky inner planet with enough water and carbon to eventually sustain life, and sufficient mass to hold on to volatile components over the eons. Earth's sister planets, Venus and Mars, formed from similar ingredients but evolved along different pathways – one a cold, dry desert, the other scorched by a runaway greenhouse atmosphere. Much of what we know of how the Solar System formed and planets developed within it comes from geochemical studies of meteorites – pieces of asteroids whose composition and mineralogy has been preserved over four and a half billion years. Scientific study of meteorites was initiated in the early nineteenth century by chemists such as Edward Charles Howard, Jöns Jacob Berzelius, and Charles Barthold. In the subsequent two centuries, a great deal has been learned about the birth of the Solar System, which began as a collapsing, spinning nebula of gas and dust, much as Immanuel Kant had proposed in 1755.

Chondritic meteorites are composed of collections of this nebular dust, some of which, the calcium-aluminum inclusions or CAI's, condensed from nebula gas at temperatures above 1400 K, perhaps in transient heating events as the material cycled close to the growing Sun (118). Some dust was melted during other transient heating events, likely associated with shockwaves in the nebula, to form chondrules. In contrast, the chondritic matrix, particularly in carbonaceous chondrites, condensed at far lower temperatures, likely at great distance from the Sun. The CAI's were the first material to form and one such object has been precisely dated at $4{,}568.67 \pm 0.17$ million years (119). Bulk isotopic compositions of chondritic meteorites exhibit slight variations that betray incomplete mixing between nuclides synthesized by slow neutron capture in red giant stars and ones synthesized in rapid neutron and proton capture processes in supernova explosions. Based on the presence of decay products of short-lived radionuclides, some of this material must have been synthesized only shortly before the Solar System formation and injected into the Solar System as planetesimals were already forming (120). And some chondrites preserve solids, such as SiC, graphite, diamond, and olivine (Mg_2SiO_4), that condensed from the outflow of those stars and supernovae in their fine-grained matrix (121).

In contrast to chondrites, rocky achondrites and iron meteorites are remains of disrupted asteroid-sized planetesimals that melted and differentiated into iron cores and silicate mantles. NASA's DAWN spacecraft confirmed that some of these are from the asteroid Vesta (122), which apparently formed within the first few million years of the Solar System history (123).

While much has been learned about early nebular history from chondrites and about the formation of asteroid-sized planetesimals from irons and achondrites, formation of the terrestrial planets remains poorly understood. Recent computer simulations suggest that Jupiter and Saturn, long believed to have formed early, may have drifted into the inner solar system triggering a chain of collisions that disrupted and destroyed the planetary embryos in that region, with the terrestrial planets forming from the debris once the giant planets drifted outward again (124). This so-called “Grand Tack” would have also deflected some planetesimals from the outer solar system into the inner region, supplying Earth and its system planets with the volatiles necessary for life (125).

The last major step in formation of Earth was apparently a collision between the proto-earth and a roughly Mars-sized body, named Theia, debris from which formed the Moon. The impact model explains the angular momentum of Earth–Moon system, the small size of the lunar core (the impact would have happened after Earth’s core had largely formed), and the general chemical similarity between Earth and the Moon. But that same similarity is also a problem – the two bodies are almost too similar, particularly in the isotopic compositions that vary between various solar system bodies, such as O. This requires very efficient mixing between material of the proto-earth and the impactor, which requires rather specific impact scenarios.

Certainly, much remains to be learned about Earth’s formation, and geochemistry will continue to inform that future understanding.

4. Structure, Composition, and Evolution of Earth

Cosmochemistry not only informs our understanding of Earth’s formation but also informs our understanding of Earth’s composition and evolution as well. The chemical composition of chondrites imposes important constraints on Earth’s composition. Other constraints come from its physical properties, including density, moment of inertia, and seismic wave velocities. We infer from these constraints a planet with a solid inner core with a radius of 1220 km and mean density of 12,720 kg/m^3, a liquid iron outer core of 3483 km radius and a mean density of 11,160 kg/m^3, implying a mean atomic number of ~22.8 (126). This is surrounded by a 2890 km thick mantle and crust with mean density of 4420 kg/m^3.

Magnesium–iron silicates form the bulk of chondrites and these materials have the proper density and seismic velocities to constitute Earth’s mantle when compressed under appropriate pressure. Chondrites vary in composition and no particular class of chondrites matches the earth’s composition, most critically in oxygen isotope ratios. However, a subset of elements, the most refractory ones, ie, those that would have condensed from the solar nebula at highest temperatures such as Al, Ti, Ca, Sr, the rare earths, U, and Th, are present in uniform relative abundances in all chondrite classes. A reasonable assumption is that they should be present in the same relative abundances in the earth as well. This provides a departure point for estimating Earth’s composition (eg, 127,128).

The Core. The only elements dense enough and cosmically abundant enough to form the core are iron and nickel with a Fe: Ni ratio of roughly 18: 1. However, a core of this composition would be too dense to meet geophysical constraints; thus, Fe and Ni must be alloyed with one or more lighter elements. Hydrogen, C, O, Si, and S have all been suggested as the principal light element and have been experimentally shown to partition into metallic liquids under certain conditions of temperature, pressure, oxygen fugacity, and composition (129). Since the conditions of core–mantle equilibration are not known, which of these elements, or combination of them, accounts for the low-mean atomic number of the core is unclear. Many other elements, notably Goldschmidt's siderophile elements, are undoubtedly highly concentrated in the earth's core as well, which explains their rarity in the silicate Earth. The concentrations of these elements in the core can be estimated from their deficit in the silicate part of Earth. Thus, for example, the average concentration of Pt in chondrites is about 1.3 ppm, but the silicate Earth contains only ~0.007 ppm, implying 5.7 ppm in the core (eg, 130).

The very old ages of iron meteorites indicate that core segregation likely had already occurred in the planetary embryos that accreted to form Earth, with the Moon-forming impact likely the last opportunity for metal separation. The abundance of ^{182}W, the product of the extinct radionuclide ^{182}Hf ($t_{1/2} = 8.9$ million years) in the earth's mantle and in lunar rocks constrains the timing of this event to be roughly 60 million years after formation of the CAI's (131).

The earth's core was very likely initially entirely liquid, with the inner core, which constitutes only 5% of its mass, slowly crystallizing from it. Just when this crystallization began is uncertain. The latent heat generated by this process may be an important source of energy to generate Earth's magnetic field. Earth's magnetic field has been present for at least 3.4 billion years (132), so if the geodynamo is connected to inner core crystallization, it must have begun by then, but others have argued for a much younger inner core (133).

The Crust. While Earth's core undoubtedly formed early, the crust has formed through partial melting of the mantle and magmatism over geologic time. The continental crust compositionally heterogeneous but is overall richer in aluminosilicates than the mantle and oceanic crust.

Although crust formation began more than 4 billion years ago, its average age is much younger, perhaps 2 billion years and the pace of the continent creation has long been debated and remains contentious. Some have argued for a nearly steady-state crustal mass for the last 4 billion years (134), while others argue that little continental crust was present until the earth reached middle age around 2.7 billion years ago (135). Certainly, there is relatively little crust older than 3 billion years; the argument centers on how effectively crust can be destroyed and recycled into the mantle. There does seem to be broad, although not universal, agreement on two important points. First, The crust shows peaks in U–Pb zircon ages around 2700, 1900, 1000, and 600 million years ago, which are variably interpreted as episodes of crustal growth (eg, 136) or peaks in preservation (eg, 135,137). Second, the composition of newly added crust underwent a distinct change near the end of the Archean around 2.5 billion years ago, becoming richer in SiO_2, and elements such as K and Rb and poorer in elements such as Mg and Ni (138). Why this change occurred is debated, but some argue it reflects the beginning of modern-style plate tectonics (eg, 139).

The distinctive trace element composition of continental crust, notably its strong enrichment in elements such as Rb, Ba, K, and Pb and relative depletion in Nb and Ta, suggest much of the continental crust was produced by supra-subduction zone magmatism (140). As are subduction zone magmas, continental crust is andesitic on average in composition. But andesites are not common in the crust and andesitic magmas are not generated directly by partial melting of the mantle but rather evolve from basaltic ones through fractional crystallization. This "crustal composition paradox" indicates the continents have attained their composition through additional refining processes. This could include loss of weathering products to the mantle through subduction, melts derived from subducting oceanic crust, and recycling of the dense lower crust through density foundering or relamination (eg, 140,141,142).

5. Geochemical Techniques and Instrumentation

Geochemists use a great variety of instrumentation. Unlike a compound created in a chemistry laboratory, the composition of the material of interest is often not known, so instrumentation and techniques to characterize samples' composition are particularly important. Over the last 50 years, spectroscopic analytical techniques have become dominant. X-ray fluorescence (XRF) and inductively coupled plasma–atomic emission spectroscopy (ICP-AES) have largely replaced older techniques for determining bulk elemental abundances, the former particularly suited for solids and the latter for both liquids and solids. Portable and compact XRF units are used in minerals exploration and are part of the instrument package of Martian rovers. For trace elements, inductively coupled plasma–mass spectrometry (ICP-MS), introduced in the 1980's, has become the method of choice in many cases. A variety of methods have been developed for sample introduction to ICP instruments beyond the traditional solution aspiration method, including laser ablation, hydride generation, and electrothermal vaporization. Neutron activation analysis, introduced in the 1950's, remains widely used, particularly for elements such as Ir in K-Pg boundary clays (48) that are difficult to analyze by other methods. The simplicity and accuracy with which rare earths are analyzed by this technique partly explains geochemists' intense interest in this group of elements. For organic materials, mass spectrometry combined with various chromatographic techniques is predominant, as it is in other fields of organic chemistry. A range of spectrographic techniques based on absorbance, reflectance, and emittance are also in common used. For example, the minerals and petroleum industry common use wire-line gamma ray spectrometers to determine K, U, and Th as a function of depth in drill holes and gamma ray spectrometers are commonly part of the instrument package aboard planetary exploration spacecraft. At the other end of the electromagnetic spectrum, IR absorption spectroscopy is used to determine the water content of volcanic glasses and to routinely measure atmospheric greenhouse gas concentrations continuously, in discrete samples, and from aircraft and satellites. Reflectance spectroscopy, both from ground-based telescopes and spacecraft, is used to investigate the mineralogical and chemical composition of planetary and asteriodal surfaces (eg, 143).

Other techniques are used to characterize other aspects such as crystal structure or speciation in solutions. X-ray diffraction has a century-long history of use to determine the crystal structure of minerals and for mineral identification. UV-visible spectroscopy can be used to characterize transition metal complexation in solution (eg, 144). Raman spectroscopy provides direct information about the bonding state of a material through the observations of elementary vibrational excitations and is used for crystalline phase identification and structural analysis, detection of phase transformations such as melting in experiments, and determination of elastic and thermodynamic properties. Mössbauer spectroscopy provides information on valence and spin states, ligand symmetry, magnetism, and lattice dynamics. Luminescence spectroscopy can provide information on the presence of trace elements and crystallite growth and zoning.

Geochemists also make use of a wide variety of instrumentation to investigate materials at very fine scales. Electron microprobes are used to determine elemental composition at the micron scale, but this technique is limited to the more abundant elements. Trace element abundances can be determined at fine scales using secondary ion mass spectrometers (SIMS), also called ion microprobes, or through laser ablation ICP-MS. Geochemists also make use of X-ray adsorption near-edge structure analysis (XANES) to interrogate the chemical state, such as valence state, coordination number, and bonding distances of atoms in soil minerals, volcanic glasses. At very fine scales, synchrotron X-ray diffraction, XRF, and proton-induced X-ray emission spectroscopy (PIXE) provides structural and compositional analysis. Electron and atomic force microscopy are used to study mineral surfaces and reactions at them.

Isotope ratio measurements have traditionally been performed with either thermal ionization or gas source magnetic sector mass spectrometers. While the magnetic sector design remains necessary for high precision isotope ratios, new ion source designs have diversified these instruments. Most important are ICP-MS and secondary ionization ion sources. The former is particularly useful for elements with poor thermal ionization efficiencies, eg, Hf, Th. High-resolution secondary ion mass spectrometers can be used for very fine scale measurements of both stable and radiogenic isotope ratios, as can the former when combined with laser ablation. Indeed, the oldest age of any terrestrial material, 4.4 billion years, was determined on a zircon crystal with a SIMS instrument (145). Accelerator mass spectrometry is routinely used for quantification of very rare isotopes such as ^{14}C and ^{10}Be, partly supplanting β-counting. Many of the techniques described here are used in combination; for example, catholuminescence is used to identify and characterize zoning in zircons prior to analysis by SIMS for U–Pb dating.

Geochemists also work extensively with thermodynamic models, and there are a variety of available computer codes and programs. They have in common the fundamental principle that the equilibrium state of a system is the one with the lowest Gibbs free energy and hence attempt to determine the phases and their compositions that exist at equilibrium if the composition, temperature, and pressure of a system are specified. Models for low-temperature aqueous geochemistry are used for a wide variety of problems, ranging through seawater speciation, low-temperature ore deposition, nuclear waste storage, municipal, industrial, and mine waste management, and environmental remediation, have been recently reviewed by Nordstrom and Campbell (146). Other codes are available for metamorphic, magmatic, and mantle geochemistry, such as THERMOCALC (63,147,148), MELTS (60), and Perple_X (149). Increasingly, *ab initio* calculations are used as well (eg, 69,150,151).

Experiments at the time and volume scales of the earth are, of course, impossible (although it could be argued than humanity is now engaged in one, the results of which appear to confirm the predications made by Arrhenius (1) more than a century ago), but smaller scale experiments are an integral part of geochemistry. Indeed, thermodynamic models discussed above require thermodynamic data that must be acquired through experiments. Experiments in low-temperature geochemistry are sometimes not greatly different than ones that would be conducted in other research chemistry laboratories. Experiments at the pressures and temperatures of the earth's interior require much more specialized apparatus and instrumentation. Of particular note is the diamond-anvil cell (152), in which samples (albeit tiny) can be subjected to pressures and temperatures corresponding to those of the earth's lower mantle and core and analyzed in combination with techniques such as synchrotron X-ray diffraction probe their properties (153,154).

BIBLIOGRAPHY

CITED PUBLICATIONS

1. S. Arrhenius, *Proc. R. Swedish Acad. Sci.*, **22**, 1–101 (1896).
2. R. A. Berner, A. C. Lasaga, R. M. Garrells, *Am. J. Sci.*, **283**, 641–683 (1983).
3. R. A. Berner, *Geochim. Cosmochim. Acta*, **70**, 5653–5664 (2006).
4. W. S. Broecker and G. H. Denton, *Geochim. Cosmochim. Acta*, **53**, 2465–2501 (1989).
5. W. Broecker, *Geochem. Perspect.*, **1**, 221–221 (2012).
6. H. Krough, in C. Reinhardt, ed., *Chemical Sciences in the 20th Century: Bridging Boundaries*, Wiley-VCH Verlag GmbH, Weinhiem, 2001, pp. 160–192.
7. G. Bischof, *Lehrbuch der chemischen und physikalischen Geologie*, A. Marcus, 1847.
8. F. W. Clarke, *US Geol. Surv. Bull*, 770 (1908).
9. V. M. Goldschmidt, *Naturwissenschaften*, **7**, 105–123 (1922).
10. V. I. Vernadsky, *Biosfera (The Biosphere); Nauchnoe khimiko-technicheskoye izdatel'stvo*, Leningrad, 1926.
11. S. L. Brantley, and co-workers, *Frontiers in Exploration of the Critical Zone*, National Science Foundation, Newark, DE, 2006.
12. J. Chorover and co-workers, *Elements*, **3**, 321–326 (2007).
13. W. M. White, *Geochemistry*, Wiley-Blackwell, Oxford, 2013.
14. U. Siegenthaler, J. L. Sarmiento, *Nature*, **365**, 119–125 (1993).
15. P. Falkowski and co-workers, *Science*, **290**, 291–296 (2000).
16. T. F. Stocker and co-workers, Cambridge University PressCambridge, 2014.
17. J. Kasting, *Science*, **259**, 920–926 (1993).
18. H. D. Holland, in A. E. J. Engle, H. L. James, and B. F. Leonard, eds., *Petrologic Studies A Volume to Honor AE Buddington*, Geological Society of America, New York, 1962, pp. 447–477.
19. H. D. Holland, *Philos. Trans. R. Soc. B Biol. Sci.*, **361**, 903–915 (2006).
20. J. Farquhar, H. Bao, and M. Thiemens, *Science*, **289**, 756–758 (2000).
21. J. F. Kasting and D. Catling, *Annu. Rev. Astron. Astrophys.*, **41**, 429–463 (2003).
22. T. W. Lyons, C. T. Reinhard and N. J. Planavsky, *Nature*, **506**, 307–315 (2014).
23. H. D. Holland, *Geochim. Cosmochim. Acta*, **73**, 5241–5255 (2009).
24. F. Gaillard, B. Scaillet and N. T. Arndt, *Nature*, **478**, 229–232 (2011).
25. W. W. Fischer, J. Hemp, and J. E. Johnson, *Annu. Rev. Earth Planet. Sci.*, **44**, 647–683 (2016).
26. D. E. Canfield, S. W. Poulton, and G. M. Narbonne, *Science*, **315**, 92–95 (2007).
27. A. Bekker and co-workers, *Econ. Geol.*, **105**, 467–508 (2010).
28. K. S. Johnson, R. M. Gordon, and K. H. Coale, *Mar. Chem.*, **57**, 137–161 (1997).
29. M. Kleber and M. G. Johnson, in L. S. Donald, ed., *Advances in Agronomy*, Academic Press. 2010, pp. 77–142.
30. M. W. I. Schmidt and co-workers, *Nature*, **478**, 49–56 (2011).
31. W. J. Parton and co-workers, *Soil Sci. Soc. Am. J.*, **51**, 1173–1179 (1987).

32. K. Lalonde and co-workers, *Nature*, **483**, 198–200 (2012).
33. A. Treibs, *Justus Liebigs Ann. Chem.*, **510**, 42–62 (1934).
34. K. E. Peters, C. C. Walters, and J. M. Moldowan, *The Biomarker Guide: Volume 2, Biomarkers and Isotopes in Petroleum Systems and Earth History*, Cambridge University Press, Cambridge, 2007.
35. M. G. Carls, and co-workers, *Environ. Toxicol. Chem.*, **35**, 2683–2690 (2016).
36. D. E. G. Briggs and R. E. Summons, *BioEssays*, **36**, 482–490 (2014).
37. M. Pagani and co-workers, *Science*, **334**, 1261–1264 (2011).
38. M. Pagani, M. A. Arthur, and K. H. Freeman, *Paleoceanography*, **14**, 273–292 (1999).
39. T. I. Eglinton and G. Eglinton, *Earth Planet. Sci. Lett.*, **275**, 1–16 (2008).
40. A. Lavoisier, *Mem. Acad. Roy. Sci. (Paris)*, **1772**, 555–563 (1772).
41. E. A. Boyle, J. M. Edmond, and E. R. Sholkovitz, *Geochim. Cosmochim. Acta*, **41**, 1313–1324 (1977).
42. G. Forchhammer, *J. Franklin Inst.*, **74**, 401–403 (1862).
43. W. Dittmar, *Chem. Phys.*, **1**, 1–211 (1884).
44. J. B. Corliss, and co-workers, *Science*, **203**, 1073–1083 (1979).
45. E. A. Boyle, R. F. Anderson, G. A. Cutter, R. Fine, W. J. Jenkins, and M. Saito, eds., *GEOTRACES GA-03 - The U. S. GEOTRACES North Atlantic Transect*, Elsevier, Amsterdam, 2015; Vol. 116.
46. J. F. Adkins, *Paleoceanography*, **28**, 539–561 (2013).
47. H. C. Wu and co-workers, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **412**, 208–222 (2014).
48. L. W. Alvarez and co-workers, *Science*, **208**, 1095–1108 (1980).
49. J. Punekar and co-workers, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **441**, 116–136 (2016).
50. G. Artioli and S. Quartieri, *Elements*, **12**, 13–18 (2016).
51. T. Carter and co-workers, *J. Archaeol. Sci.*, **33**, 893–909 (2006).
52. L. M. Mallory-Greenough and co-workers, *Archaeometry*, **41**, 227–238 (1999).
53. A. Shortland, N. Rogers, and K. Eremin, *J. Archaeol. Sci.*, **34**, 781–789 (2007).
54. A. M. Pollard and P. J. Bray, *Archaeometry*, **57**, 996–1008 (2015).
55. M. I. Weisler and co-workers, *Proc. Natl. Acad. Sci.*, **113**, 8150–8155 (2016).
56. R. A. Bentley, *J. Anthropol. Archaeol.*, **32**, 303–312 (2013).
57. W. Müller and co-workers, *Science*, **302**, 862–866 (2003).
58. P. B. de Menocal, *Science*, **331**, 540–542 (2011).
59. S. A. Bowring and I. S. Williams, *Contrib. Mineral. Petrol.*, **134**, 3–16 (1999).
60. M. S. Ghiorso and co-workers, *Geochem., Geophys., Geosyst.*, **3**, 1030 (2002).
61. N. L. Bowen, *The Evolution of the Igneous Rocks*, Princeton University Press, Princeton, 1928.
62. F. S. Spear, *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*, Mineralogical Society of America, Washington, 1995.
63. T. J. B. Holland, and R. Powell, *J. Metamorphic Geol.*, **29**, 333–383 (2011).
64. J. B. Thomas and co-workers, *Contrib. Mineral. Petrol.*, **169**, 1–16 (2015).
65. S. D. Scott, in *Teartise on Geochemistry*, H.D. Holland and K.K. Turekian, eds, Vol. 13, Elsevier, Amsterdam, 2014, pp. 650.
66. G. Agricola, *De Re Metallica*, ed., Dover, New York, 1950, p. 1556.
67. S. P. Ogryzlo, *Econ. Geol.*, **30**, 400–424 (1935).
68. Z. Zajacz and co-workers, *Earth Planet. Sci. Lett.*, **297**, 50–56 (2010).
69. X. Liu and co-workers, *Geochim. Cosmochim. Acta*, **75**, 185–194 (2011).
70. G. S. Pokrovski, N. N. Akinfiev, A. Y. Borisova, A. V. Zotov, and K. Kouzmanov, Geological Society, London, Special Publications, 2014, **402**, pp. 9–70.
71. A. E. Williams-Jones, R. J. Bowell, and A. A. Migdisov, *Elements*, **5**, 281–287 (2009).

72. S. Jégo and co-workers, *Geochim. Cosmochim. Acta*, **188**, 224–243 (2016).
73. J. L. Walshe and J. S. Cleverley, *Elements*, **5**, 288 (2009).
74. R. J. Herrington and J. J. Wilkinson, *Geology*, **21**, 539–542 (1993).
75. M. Hannington and co-workers, *Nat. Geosci.*, **9**, 299–302 (2016).
76. D. L. Kelley and co-workers, *Econ. Geol.*, **101**, 729–752 (2006).
77. K. Kyser, J. Barr, and C. Ihlenfeld, *Elements*, **11**, 241–246 (2015).
78. W. Fyfe, *Science*, **213**, 105–110 (1981).
79. R. A. Jr.Davis, and co-workers, *Environment. Geol.*, **39**, 1107–1116 (2000).
80. S. E. Fawcett and H. E. Jamieson, *Chem. Geol.*, **283**, 109–118 (2011).
81. B. B. Boltwood, *Am. J. Sci. Ser. 4* **23**, 77–88 (1907).
82. A. O. Nier, R. W. Thompson, B. F. Murphey, *Phys. Rev.*, **60**, 112–116 (1941).
83. C. Patterson, *Geochim. Cosmochim. Acta*, **16**, 230–237 (1956).
84. P. R. Renne and co-workers, *Science*, **339**, 684–687 (2013).
85. K. A. Farley and co-workers, *Science*, 343 (2014).
86. W. M. White, *Isotope Geochemistry*, John Wiley & Sons, Inc., 2015.
87. F. Albarède, S. L. Goldstein, and D. Dautel, *Geochim. Cosmochim. Acta*, **61**, 1277–1291 (1997).
88. R. L. Armstrong, *Earth Planet. Sci. Lett.*, **12**, 137–142 (1971).
89. R. L. Armstrong, *Rev. Geophys.*, **6**, 175–199 (1968).
90. W. M. White and A. W. Hofmann, *Nature*, **296**, 821–825 (1982).
91. F. Tera and co-workers, *Geochim. Cosmochim. Acta*, **50**, 535–550 (1986).
92. H. C. Urey, *J. Chem. Soc.*, **1947**, 562–581 (1947).
93. J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).
94. C. M. Johnson, B. L. Beard, and F. Albarede, eds., *Geochemistry of Non-Traditional Stable Isotopes*, Mineralogical Society of America, Washington, DC, 2004, Vol. 55.
95. C. Emiliani, *J. Geol.*, **63**, 538–578 (1955).
96. J. Jouzel and co-workers, *Nature*, **329**, 403–408 (1987).
97. J. Jouzel and co-workers, *Science*, **317**, 793–796 (2007).
98. E. G. Nisbet, D. P. Mattey, D. Lowry, *Nature*, **367**, 694–694 (1994).
99. M. Rosing, *Science*, **283**, 674–676 (1999).
100. A. P. Nutman and co-workers, *Nature, advance online publication*, **537**, 535–538 (2016).
101. D. A. Hodell and co-workers, *Geochem. Geophys. Geosyst.*, **4**, 1004 (2003).
102. S. d'Hondt and co-workers, *Science*, **282**, 276–278 (1998).
103. Y. Li and J. Liu, *Geochim. Cosmochim. Acta*, **70**, 1789–1795 (2006).
104. N. Dauphas and E. A. Schauble, *Annu. Rev. Earth Planet. Sci.*, **44**, 709–783 (2016).
105. J. W. Jamieson and co-workers, *Econ. Geol.*, **101**, 1055–1061 (2006).
106. M. K. Deakin, G. Beaudoin, and M. Malo, *Ore Geol. Rev.*, **66**, 1–24 (2015).
107. R. N. Clayton, N. Onuma, and T. S. Mayeda, *Earth Planet. Sci. Lett.*, **30**, 10–18 (1976).
108. R. N. Clayton, *Nature*, **415**, 860–861 (2002).
109. J. R. Lyons, *Geophys. Res. Lett.*, **34**, L22811 (2007).
110. J. Farquhar and co-workers, *Science*, **298**, 2369–2372 (2002).
111. R. A. Cabral and co-workers, *Nature*, **496**, 490–493 (2013).
112. H. Delavault and co-workers, *Proc. Natl Acad. Sci.*, **113**, 12952–12956 (2016).
113. S. W. French and B. Romanowicz, *Nature*, **525**, 95–99 (2015).
114. W. M. White, *Chem. Geol.*, **419**, 10–28 (2015).
115. D. Porcelli, C. Ballentine, R. Weiler, eds., *Noble Gases in Geochemistry and Cosmochemistry*, Mineralogical Society of America, Washington, 2002, Vol. 47.
116. M. Moreira, *Geochem. Perspect.*, **2**, 229–230 (2013).
117. S. Mukhopadhyay, *Nature*, **486**, 101–104 (2012).
118. A. N. Krot and co-workers, *Geochim. Cosmochim. Acta*, **73**, 4963–4997 (2009).

119. A. Bouvier and M. Wadhwa, *Nat. Geosci.*, **3**, 637–641 (2010).
120. M. Bizzarro and co-workers, *Science*, **316**, 1178–1181 (2007).
121. T. Ming and E. Anders, *Geochim. Cosmochim. Acta*, **52**, 1235–1244 (1988).
122. M. C. De Sanctis and co-workers, *Science*, **336**, 697–700 (2012).
123. L. E. Nyquist and co-workers, *Earth Planet. Sci. Lett.*, **214**, 11–25 (2003).
124. K. Batygin and G. Laughlin, *Proc. Natl. Acad. Sci.*, **112**, 4214–4217 (2015).
125. A. Morbidelli and co-workers, *Ann. Rev. Earth Planet. Sci.*, **40**, 251–275 (2012).
126. F. Birch, *Phys. Earth Planet. Inter.*, **1**, 141–147 (1968).
127. W. F. McDonough and S. S. Sun, *Chem. Geol.*, **120**, 223–253 (1995).
128. H. Palme and H. S. C. O'Neill, in H. D. Holland and H. K. Turekian, ed., *Treatise on Geochemistry*, 2nd ed., Elsevier, Oxford, 2014, pp. 1–39.
129. R. A. Fischer and co-workers, *Geochim. Cosmochim. Acta*, **167**, 177–194 (2015).
130. W. F. McDonough, in ed., *Treatise on Geochemistry*2nd edn, Elsevier. Oxford, 2014, pp. 559–577.
131. M. Touboul and co-workers, *Nature*, **450**, 1206–1209 (2007).
132. J. A. Tarduno and co-workers, *Science*, **327**, 1238–1240 (2010).
133. S. Labrosse, *Phys. Earth Planet. Inter.*, **247**, 36–55 (2015).
134. R. L. Armstrong, in S. Moorbath, and B. F. Windley, eds., *The Origin and Evolution of the Earth's Continental Crust*, The Royal Society, London, 1981, pp. 259–287.
135. K. C. Condie and R. C. Aster, *Precambrian Res.*, **180**, 227–236 (2010).
136. N. T. Arndt, *Geochem. Perspect.*, **2**, 405–405 (2013).
137. C. J. Hawkesworth and A. I. S. Kemp, *Chem. Geol.*, **226**, 134–143 (2006).
138. S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution*, 1st ed., Blackwell Scientific Publications, Oxford, 1985.
139. B. Dhuime, A. Wuestefeld, and C. J. Hawkesworth, *Nat. Geosci.*, **8**, 552–555 (2015).
140. R. L. Rudnick and S. Gao, in H. D. Holland, and K. K. Turekian, eds., *Treatise on Geochemistry*, 2nd edn, Elsevier. Oxford, 2014, pp. 1–51.
141. H. Rollinson, *Geochem. Geophys. Geosyst.*, **9**, Q12010 (2008).
142. B. R. Hacker, P. B. Kelemen, and M. D. Behn, *Earth Planet. Sci. Lett.*, **307**, 501–516 (2011).
143. M. C. De Sanctis and co-workers, *Nature*, **536**, 54–57 (2016).
144. A. Usher, D. C. McPhail, and J. Brugger, *Geochim. Cosmochim. Acta*, **73**, 3359–3380 (2009).
145. S. A. Wilde and co-workers, *Nature*, **409**, 175–178 (2001).
146. T. Xu and co-workers, *Am. J. Sci.*, **301**, 34–59 (2001).
147. R. Powell, T. Holland, and B. Worley, *J. Metamorphic Geol.*, **16**, 577–588 (1998).
148. R. Powell and T. J. B. Holland, *J. Metamorphic Geol.*, **26**, 155–179 (2008).
149. J. A. D. Connolly, *Earth Planet. Sci. Lett.*, **236**, 524–541 (2005).
150. Y. Lin, R. Cohen, A. Floris, L. Shulenburger, and K. P. Driver, *APS Meeting Abstracts*, 2016.
151. M. Javoy and co-workers, *Earth Planet. Sci. Lett.*, **319–320**, 118–127 (2012).
152. L. Merrill, W. A. Bassett, *Rev. Scientific Instrum.*, **45**, 290–294 (1974).
153. S. Anzellini and co-workers, *Science*, **340**, 464–466 (2013).
154. K. Ohta and co-workers, *Earth Planet. Sci. Lett.*, **349–350**, 109–115 (2012).

FURTHER READING

H. D. Holland and K. Turekian eds., *Treatise on Geochemistry*2nd edn, Elsevier, Amsterdam, 2014, 15 volumes. http://www.sciencedirect.com/science/referenceworks/9780080983004

S. D. Killops and V. J. Killops, *An Introduction to Organic Geochemistry*, Longman Scientific and Technical, Essex. 1993.

H. Y. McSween and G. R. Huss, *Cosmochemistry*, Cambridge University Press, Cambridge. 2010.

W. M. White, *Geochemistry*, Wiley-Blackwell, Oxford. 2013.

W. M. White, *Isotope geochemistry*, John Wiley & Sons, Inc., Oxford. 2015.

W. M. White (ed.), *Encyclopedia of Geochemistry*, Springer, Heidelberg. 2017. http://link.springer.com/referencework/10.1007/978-3-319-39193-9

William M. White
Cornell University, Ithaca, NY, USA