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REVIEW PAPER

Mineral evolution

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ABSTRACT

The mineralogy of terrestrial planets evolves as a consequence of a range of physical, chemical, and biological processes. In pre-stellar molecular clouds, widely dispersed microscopic dust particles contain approximately a dozen refractory minerals that represent the starting point of planetary mineral evolution. Gravitational clumping into a protoplanetary disk, star formation, and the resultant heating in the stellar nebula produce primary refractory constituents of chondritic meteorites, including chondrules and calcium-aluminum inclusions, with ~60 different mineral phases. Subsequent aqueous and thermal alteration of chondrites, asteroidal accretion and differentiation, and the consequent formation of achondrites results in a mineralogical repertoire limited to ~250 different minerals found in unweathered meteorite samples.

Following planetary accretion and differentiation, the initial mineral evolution of Earth's crust depended on a sequence of geochemical and petrologic processes, including volcanism and degassing, fractional crystallization, crystal settling, assimilation reactions, regional and contact metamorphism, plate tectonics, and associated large-scale fluid-rock interactions. These processes produced the first continents with their associated granitoids and pegmatites, hydrothermal ore deposits, metamorphic terrains, evaporites, and zones of surface weathering, and resulted in an estimated 1500 different mineral species. According to some origin-of-life scenarios, a planet must progress through at least some of these stages of chemical processing as a prerequisite for life.

Biological processes began to affect Earth's surface mineralogy by the Eoarchean Era (~3.85–3.6 Ga), when large-scale surface mineral deposits, including banded iron formations, were precipitated under the influences of changing atmospheric and ocean chemistry. The Paleoproterozoic "Great Oxidation Event" (~2.2 to 2.0 Ga), when atmospheric oxygen may have risen to >1% of modern levels, and the Neoproterozoic increase in atmospheric oxygen, which followed several major glaciation events, ultimately gave rise to multicellular life and skeletal biomineralization and irreversibly transformed Earth's surface mineralogy. Biochemical processes may thus be responsible, directly or indirectly, for most of Earth's 4300 known mineral species.

The stages of mineral evolution arise from three primary mechanisms: (1) the progressive separation and concentration of the elements from their original relatively uniform distribution in the pre-solar nebula; (2) an increase in range of intensive variables such as pressure, temperature, and the activities of H_2O, CO_2, and O_2; and (3) the generation of far-from-equilibrium conditions by living systems. The sequential evolution of Earth's mineralogy from chondritic simplicity to Phanerozoic complexity introduces the dimension of geologic time to mineralogy and thus provides a dynamic alternate approach to framing, and to teaching, the mineral sciences.

Keywords: Pre-solar minerals, meteorite minerals, biominerals, organominerals, teaching mineralogy

INTRODUCTION

Earth today boasts about 4300 known species of minerals, with as many as 50 new types being identified each year (e.g., http://rruff.info/ima). Yet the mineralogical diversity now found at or near Earth's surface, defined here as micro- or macroscopic solid phases (>1 μm diameter) at crustal depths less than about 3 km (i.e., where direct interaction with microbial life is likely), was not present for much of the planet's history. Indeed, both the variety and relative abundances of near-surface minerals have changed dramatically over more than 4.5 billion years of Earth history through a variety of physical, chemical, and biological processes.

Our principal objective is to explore the nature of mineral evolution by reviewing significant episodes of change in the diversity and distribution of minerals on Earth (Table 1 and Fig. 1). Thousands of previous publications document specific aspects of Earth's mineral evolution, from the pre-planetary alteration of

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primitive chondritic meteorites, through igneous, metamorphic and sedimentary petrology, to metazoan biomineralization of the Phanerozoic Era. However, few attempts have been made to synthesize these mineralogical data into a coherent chronology (see, however, Wenk and Bulakh 2004, p. 594–595; Hazen 2008, p. 4–6). The concept of mineral evolution provides an important perspective on Earth's history and a potentially useful framework for teaching mineralogy. Furthermore, it may prove particularly useful in attempts to understand chemical aspects of life's origins, as well as the development of quantitative measures for comparative planetology and the search for other living worlds.

Earth's history is a continuum, yet several significant irreversible mineralogical events, each triggered by new physical, chemical and/or biological processes, have been recognized in the geological record and provide a chronological framework for this overview. These processes diversified Earth's mineralogy in three ways. First, they increased the range of bulk compositions from which minerals form, from the original, relatively uniform composition of the solar nebula. Second, geological processes increased the range of physical and chemical conditions under which minerals form from a given bulk composition (e.g., P, T, a_{H_2O}, a_{CO_2}, a_{O_2}, etc.). Third, living organisms opened up new reaction pathways by which minerals formed that were not accessible in the abiotic world.

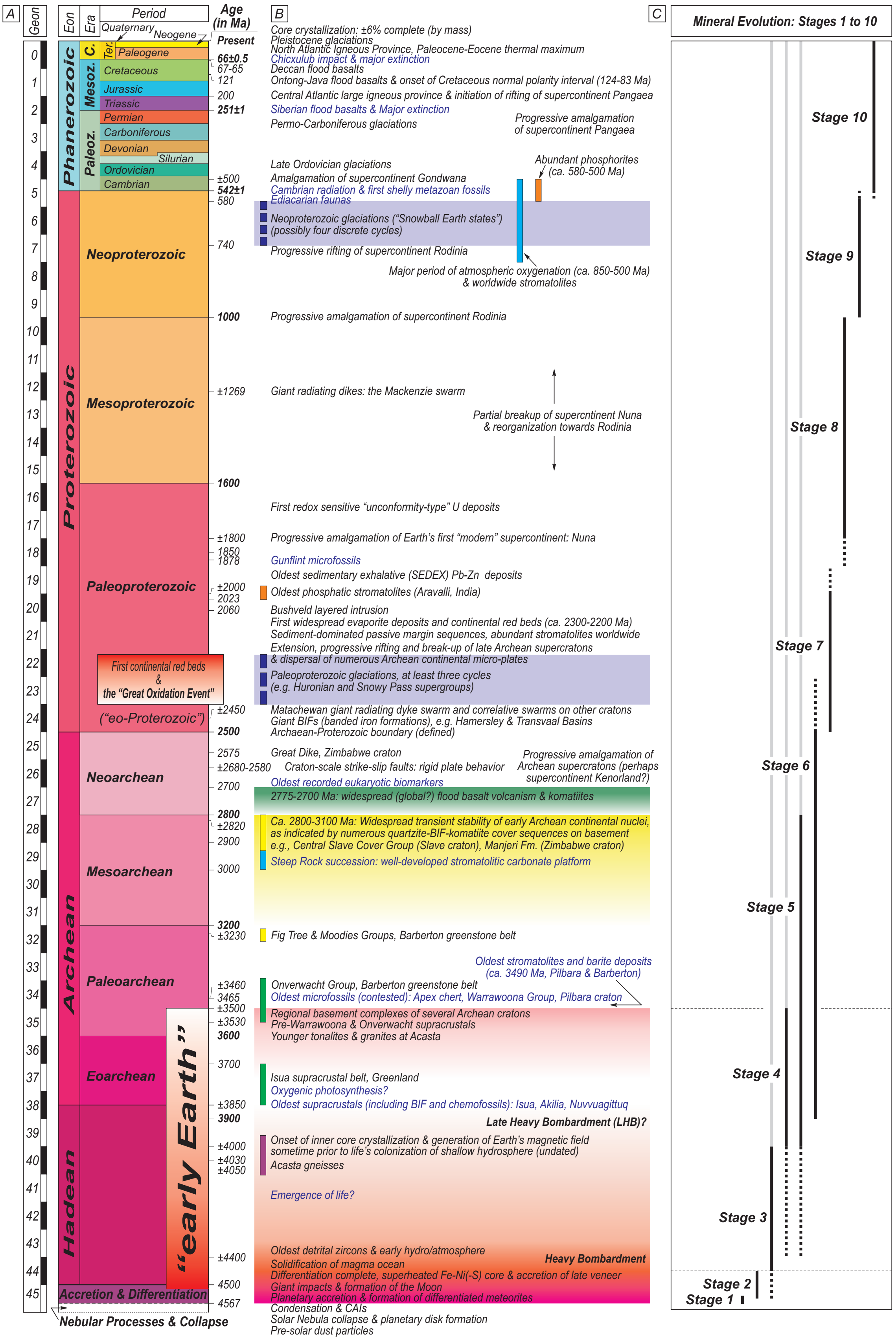
In particular, Earth has experienced three broad eras of mineral evolution, which can be further subdivided into 10 partially overlapping stages (Table 1; Fig. 1), each of which saw the expansion of mineralogical diversity and/or variation in relative mineral abundances. The first era began with the extreme mineralogical simplicity of pre-stellar "dense" molecular clouds, in which widely dispersed microscopic dust particles contained only about a dozen known refractory oxides, carbides, nitrides, and silicates that represent the starting point of mineral evolution. Gravitational clumping into a protoplanetary disk, star formation, and the resultant heating in the solar nebula produced the distinctive chondrules and calcium-aluminum inclusions that dominate chondritic meteorites, which incorporate ~60 primary mineral phases that formed by direct condensation, melt solidification, or solid-state recrystallization. Subsequent aqueous and thermal alteration of chondrites led to dozens of

►**FIGURE 1.** Geologic time scale (**a**), major events and milestones in Earth evolution (**b**), and the 10 stages of mineral evolution discussed in this paper (**c**). The main time intervals of the mineral stages, which represent significant developments in terms of mineral diversity, are indicated with solid vertical lines; less certain initiations of these stages, or gradual transitions, are indicated with dotted vertical lines; gray vertical lines indicate continuation to the present of key processes associated with some of the mineral stages. Figure adapted from Bleeker (2004); eon, era, and period terminology of the time scale follows Gradstein et al. (2004); the "Geon" scale on the left provides a convenient shorthand for 100 million year time intervals, after Hoffman (1990).

TABLE 1. Ten stages of mineral evolution of terrestrial planets, with possible timing on Earth, examples of minerals, and estimates of the cumulative number of different mineral species

Stage	Age (Ga)	Examples of minerals	~ Cumulative no. species
The era of planetary accretion (>4.55 Ga)			
1. Primary chondrite minerals	>4.56 Ga	Mg-olivine/pyroxene, Fe-Ni metal, FeS, CAIs	60
2. Planetesimal alteration/differentiation	>4.56 to 4.55 Ga		250
a) aqueous alteration		phyllosilicates, hydroxides, sulfates, carbonates, halite	
b) thermal alteration		albite, feldspathoids, biopyriboles	
c) shock phases		ringwoodite, majorite, akimotoite, wadsleyite	
d) achondrites		quartz, K-feldspar, titanite, zircon	
e) iron meteorites		many transition metal sulfides and phosphates	
The era of crust and mantle reworking (4.55 to 2.5 Ga)			
3. Igneous rock evolution	4.55 to 4.0 Ga		350 to 500
a) fractionation		feldspathoids, biopyriboles (volatile-poor planets)	350
b) volcanism, outgassing, surface hydration		hydroxides, clay minerals (volatile-rich planets)	500
4. Granite formation	4.0 to 3.5 Ga		1000
a) granitoids		quartz, alkali feldspar (perthite), hornblende, micas, zircon	
b) pegmatites		beryl, tourmaline, spodumene, pollucite, many others	
5. Plate tectonics	>> 3.0 Ga		1500
a) hydrothermal ores		sulfides, selenides, arsenides, antimonides, tellurides, sulfosalts	
b) metamorphic minerals		kyanite, sillimanite, cordierite, chloritoid, jadeite, staurolite	
6. Anoxic biological world	3.9 to 2.5 Ga		1500
a) metal precipitates		banded iron formations (Fe and Mn)	
b) carbonates		ferroan carbonates, dolostones, limestones	
c) sulfates		barite, gypsum	
d) evaporites		halides, borates	
e) carbonate skarns		diopside, tremolite, grossularite, wollastonite, scapolite	
The era of bio-mediated mineralogy (>2.5 Ga to present)			
7. Paleoproterozoic atmospheric changes surface oxidation	2.5 to 1.9 Ga	>2000 new oxide/hydroxide species, especially ore minerals	>4000
8. Intermediate ocean	1.9 to 1.0 Ga	minimal mineralogical innovation	>4000
9. Neoproterozoic biogeochemical changes	1.0 to 0.542 Ga		>4000
a) glaciation		extensive ice deposition, but few new minerals	
b) post-glacial oxidation		extensive oxidative weathering of all surface rocks	
10. Phanerozoic Era	0.542 Ga to present		4300+
a) biomineralization		extensive skeletal biomineralization of calcite, aragonite, dolomite, hydroxylapatite, and opal	
b) bio-weathering		increased production of clay minerals, soils	

Note: The timings of some of these stages overlap and several stages continue to the present.


A
Geon
Eon
Era
Period
Age (in Ma)
Quaternary
Neogene
Present
Ter.
C.
Paleogene
66±0.5
67-65
Cretaceous
121
Mesoz.
Jurassic
200
Triassic
251±1
Permian
Carboniferous
Paleoz.
Devonian
Silurian
Ordovician
Cambrian
±500
542±1
580
Phanerozoic
Neoproterozoic
740
1000
Mesoproterozoic
±1269
1600
Proterozoic
Paleoproterozoic
±1800
1850
1878
±2000
2023
2060
First continental red beds & the "Great Oxidation Event"
("eo-Proterozoic")
±2450
2500
Neoarchean
2575
±2680-2580
2700
2800
±2820
2900
Mesoarchean
3000
3200
±3230
Paleoarchean
±3460
3465
±3500
±3530
3600
Archean
Eoarchean
3700
±3850
3900
Hadean
"early Earth"
±4000
±4030
±4050
±4400
4500
4567
Accretion & Differentiation
Nebular Processes & Collapse
0
1
2
3
4
5
6
7
8
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10
11
12
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14
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18
19
20
21
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28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
B
Core crystallization: ±6% complete (by mass)
Pleistocene glaciations
North Atlantic Igneous Province, Paleocene-Eocene thermal maximum
Chicxulub impact & major extinction
Deccan flood basalts
Ontong-Java flood basalts & onset of Cretaceous normal polarity interval (124-83 Ma)
Central Atlantic large igneous province & initiation of rifting of supercontinent Pangaea
Siberian flood basalts & Major extinction
Permo-Carboniferous glaciations
Progressive amalgamation of supercontinent Pangaea
Abundant phosphorites (ca. 580-500 Ma)
Late Ordovician glaciations
Amalgamation of supercontinent Gondwana
Cambrian radiation & first shelly metazoan fossils
Ediacarian faunas
Neoproterozoic glaciations ("Snowball Earth states") (possibly four discrete cycles)
Progressive rifting of supercontinent Rodinia
Major period of atmospheric oxygenation (ca. 850-500 Ma) & worldwide stromatolites
Progressive amalgamation of supercontinent Rodinia
Giant radiating dikes: the Mackenzie swarm
Partial breakup of supercntinent Nuna & reorganization towards Rodinia
First redox sensitive "unconformity-type" U deposits
Progressive amalgamation of Earth's first "modern" supercontinent: Nuna
Gunflint microfossils
Oldest sedimentary exhalative (SEDEX) Pb-Zn deposits
Oldest phosphatic stromatolites (Aravalli, India)
Bushveld layered intrusion
First widespread evaporite deposits and continental red beds (ca. 2300-2200 Ma)
Sediment-dominated passive margin sequences, abundant stromatolites worldwide
Extension, progressive rifting and break-up of late Archean supercratons & dispersal of numerous Archean continental micro-plates
Paleoproterozoic glaciations, at least three cycles (e.g. Huronian and Snowy Pass supergroups)
Matachewan giant radiating dyke swarm and correlative swarms on other cratons
Giant BIFs (banded iron formations), e.g. Hamersley & Transvaal Basins
Archaean-Proterozoic boundary (defined)
Great Dike, Zimbabwe craton
Craton-scale strike-slip faults: rigid plate behavior
Progressive amalgamation of Archean supercratons (perhaps supercontinent Kenorland?)
Oldest recorded eukaryotic biomarkers
2775-2700 Ma: widespread (global?) flood basalt volcanism & komatiites
Ca. 2800-3100 Ma: Widespread transient stability of early Archean continental nuclei, as indicated by numerous quartzite-BIF-komatiite cover sequences on basement e.g., Central Slave Cover Group (Slave craton), Manjeri Fm. (Zimbabwe craton)
Steep Rock succession: well-developed stromatolitic carbonate platform
Fig Tree & Moodies Groups, Barberton greenstone belt
Oldest stromatolites and barite deposits (ca. 3490 Ma, Pilbara & Barberton)
Onverwacht Group, Barberton greenstone belt
Oldest microfossils (contested): Apex chert, Warrawoona Group, Pilbara craton
Regional basement complexes of several Archean cratons
Pre-Warrawoona & Onverwacht supracrustals
Younger tonalites & granites at Acasta
Isua supracrustal belt, Greenland
Oxygenic photosynthesis?
Oldest supracrustals (including BIF and chemofossils): Isua, Akilia, Nuvvuagittuq
Late Heavy Bombardment (LHB)?
Onset of inner core crystallization & generation of Earth's magnetic field sometime prior to life's colonization of shallow hydrosphere (undated)
Acasta gneisses
Emergence of life?
Oldest detrital zircons & early hydro/atmosphere
Heavy Bombardment
Solidification of magma ocean
Differentiation complete, superheated Fe-Ni(-S) core & accretion of late veneer
Giant impacts & formation of the Moon
Planetary accretion & formation of differentiated meteorites
Condensation & CAIs
Solar Nebula collapse & planetary disk formation
Pre-solar dust particles
C
Mineral Evolution: Stages 1 to 10
Stage 10
Stage 9
Stage 8
Stage 7
Stage 6
Stage 5
Stage 4
Stage 3
Stage 2
Stage 1

Table 2. Five lists of names and idealized chemical compositions of primary minerals identified in type 3 chondrites (Rubin 1997a; Brearley and Jones 1998; Stroud et al. 2004; Ebel 2006; Messenger et al. 2006; MacPherson 2007)

Table 2a. Micro- and nano-mineral phases identified from interstellar grains in chondritic meteorites (Brearley and Jones 1998; Nittler 2003; Messenger et al. 2003; Mostefaoui and Hoppe 2004; Vollmer et al. 2007)

Name	Formula
Diamond/lonsdaleite (~2 nm)	C
Graphite	C
Moissanite	SiC
Nano-particles of TiC, ZrC, MoC, FeC, and Fe-Ni metal within pre-solar graphite	
Osbornite	TiN
Nierite	α-Si_3N_4
Rutile	TiO_2
Corundum	Al_2O_3
Spinel	$MgAl_2O_4$
Hibonite	$CaAl_{12}O_{19}$
Forsterite	Mg_2SiO_4
Perovskite structure	$MgSiO_3$
GEMS (silicate glass with embedded metal and sulfides)	

Table 2b. Primary mineral phases in chondrules of type 3.0 chondrites

Name	Formula
Forsterite	Mg_2SiO_4
Clinoenstatite	$MgSiO_3$
Orthopyroxene	$(Mg,Fe)SiO_3$
Pigeonite	$(Mg,Fe,Ca)SiO_3$
Augite	$Ca(Mg,Fe,Al)(Si,Al)_2O_6$
Anorthite	$CaAl_2Si_2O_8$
Spinel	$MgAl_2O_4$
Chromite	$FeCr_2O_4$
Ilmenite	$FeTiO_3$
Kamacite	α-(Fe,Ni) metal
Taenite	γ-(Ni,Fe) metal
Troilite	FeS
Pentlandite	$(Ni,Fe)_9S_8$
*Magnetite	Fe_3O_4
*Cohenite	$(Fe,Ni)_3C$
*Haxonite	$(Fe,Ni)_{23}C_6$
*Cristobalite/Tridymite	SiO_2
*Fayalite	Fe_2SiO_4
*Merrihueite/Roedderite	$(K,Na)_2(Fe,Mg)_5Si_{12}O_{30}$
*Pseudobrookite	Fe_2TiO_5
†Schreibersite	$(Fe,Ni)_3P$
†Perryite	$(Ni,Fe)_8(Si,P)_3$
†Oldhamite	CaS
†Niningerite	(Mg,Fe,Mn)S
†Daubreelite	$FeCr_2S_4$
†Caswellsilverite	$NaCrS_2$

* Indicates minor minerals probably formed by solid-state reaction of other phases.
† Indicates minor phases observed in chondrules of enstatite chondrites (Brearley and Jones 1998).

(continued next page)

additional minerals in chondritic meteorites. Planetesimal accretion, melting, differentiation, and impact processes yielded additional mineral phases, though no more than ~250 different minerals have been observed in unweathered meteorites. These ~250 species provided the mineralogical raw materials for Earth and other terrestrial planets.

The second era of Earth's mineral evolution was a time when elements and molecules in the crust and upper mantle were first subjected to repeated, strictly physical and chemical processing by various mechanisms. Igneous fractional crystallization, crystal settling, partial melting, and associated fluid-rock interactions resulted in radial differentiation accompanied by vertical tectonics and development of a variety of new hydrothermal, igneous, and contact metamorphic lithologies. The resulting separation and concentration of the elements, which in part reflected a gradual chemical decoupling of Earth's crust from the more reduced mantle, led to a marked diversification of the terrestrial mineral realm. In addition, lithospheric subduction and collisional zones at convergent plate boundaries and hydrothermal activity at deep-sea vents and ridges resulted in a host of new minerals associated with large-scale upper mantle and crustal reworking, massive hydrothermal ore deposits, and surface exposure of high-pressure metamorphic terrains.

The third major era of Earth's mineral evolution, which spans at least the last 3.5 billion years, is associated with biological activity and the coevolution of the geo- and biospheres. Gradual irreversible redox changes in ocean and atmospheric composition, in part mediated by surface weathering processes, carbon burial, and the episodic rise in atmospheric oxygen fostered by photosynthetic microorganisms, led to the precipitation of massive carbonates, banded iron formations, sulfates, evaporates, and other lithologies. Microbes, with their varied metabolic redox strategies, high surface reactivities that are able to concentrate metals, and ability to create and sustain chemical gradients in a variety of geochemical environments, precipitated minerals at scales from microenvironments to regional terrains. The Phanerozoic innovation of bioskeletons of carbonate, phosphate or silica resulted in new mechanisms of mineralization that continue to the modern era. The following sections examine in greater detail these evolutionary eras of mineral diversification.

The era of planetary accretion (>4.55 Ga)

The mineral evolution of terrestrial planets begins in prestellar nebulas. So called "dense molecular clouds," which are the breeding grounds of stars and their associated protoplanetary disks, are composed of gas (primarily H and He) with widely dispersed dust grains. Pre-solar interstellar grains are identified by their anomalous isotopic compositions, which point to an origin in late-stage stellar events, such as supernovae and asymptotic giant branch (AGB) stars that shed their outer envelopes. Individual interstellar grains can be recovered from the matrix of chondritic meteorites and are found to incorporate nanometer- to micrometer-sized particles of a handful of refractory minerals, including carbides, nitrides, oxides, and silicates, as recorded in Table 2a (Brearley and Jones 1998; Nittler 2003; Messenger et al. 2003, 2006; Stroud et al. 2004; Mostefaoui and Hoppe 2004; Vollmer et al. 2007). Stars and their associated planets arise through gravitational clumping of this primitive nebular material.

Stage 1. Formation of primary chondritic minerals (>4.56 Ga)

Chondrites include a variety of stony meteorites that formed early in the history of the solar nebula from the accretion of fine-grained nebular material into primitive planetesimals (Brearley and Jones 1998; Weisberg et al. 2006). The most striking features of chondritic meteorites are chondrules (Fig. 2), which are small spherical objects (typically ~1 mm in diameter) that represent molten droplets formed in space, presumably by flash heating and rapid cooling during the T-Tauri phase of the Sun's formation (Rubin 2000; Desch and Connolly 2002). Chondrites also commonly contain calcium-aluminum-rich inclusions (CAI),

TABLE 2C. Primary mineral phases in chondrite calcium-aluminum-rich inclusions (Brearley and Jones 1998; MacPherson 2007)

Name	Formula
Major phases	
Corundum	Al_2O_3
Spinel	$MgAl_2O_4$
Perovskite	$CaTiO_3$
Grossite	$CaAl_4O_7$
Hibonite	$CaAl_{12}O_{19}$
Ca-Al-oxide (spinelloid?)	$CaAl_2O_4$
Forsterite	Mg_2SiO_4
Melilite (gehlenite-akermanite solid solution)	$Ca_2Al_2SiO_7$-$Ca_2MgSi_2O_7$
Anorthite	$CaAl_2Si_2O_8$
Ca-pyroxenes	
Diopside	$CaMgSi_2O_6$
Fassaite	$CaMgSi_2O_6$-$CaAl_2SiO_6$
Rhönite	$Ca_2(Mg,Al,Ti)_6(Si,Al)_6O_{20}$
Kamacite	α-(Fe,Ni) metal
Taenite	γ-(Ni,Fe) metal
Awaruite	Ni_3Fe
Minor accessory phases (commonly << 10 μm)	
Platinum group	Pt Group element alloys
Copper	Cu,Ni,Zn alloy
Millerite	NiS
Molybdenite	MoS_2
Troilite	FeS
Pentlandite	$(Ni,Fe)_9S_8$
Rutile	TiO_2
Baddelyite	ZrO_2
Thorianite	ThO_2
Armalcolite	$(Mg,Fe)Ti_2O_5$
Magnetite	Fe_3O_4
Hercynite	$FeAl_2O_4$
Chromite	$FeCr_2O_4$
Coulsonite	FeV_2O_4
Orthoenstatite	$MgSiO_3$
Periclase (magnesiowüstite)	(Mg,Fe)O
Lime	CaO
Cohenite	Fe_3C
Cristobalite	SiO_2
Merrillite	$Ca_9NaMg(PO_4)_7$

TABLE 2D. Primary mineral phases in the fine-grained (typically <5 μm) matrix of type 3.0 chondritic meteorites (Brearley and Jones 1998)

Name	Formula
Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Clinoenstatite	$MgSiO_3$
Augite	$Ca(Mg,Fe,Al)(Si,Al)_2O_6$
Hedenbergite	$CaFeSi_2O_6$
Anorthite	$CaAl_2Si_2O_8$
Magnetite	Fe_3O_4
Chromite	$FeCr_2O_4$
Ilmenite	$FeTiO_3$
Spinel	$MgAl_2O_4$
Pentlandite	$(Ni,Fe)_9S_8$
Troilite	FeS
Pyrrhotite	$Fe_{1-x}S$
Anhydrite	$CaSO_4$
Merrillite	$Ca_9NaMg(PO_4)_7$
Kamacite	(Fe,Ni) metal
Taenite	(Ni,Fe) metal
Awaruite	Ni_3Fe
Copper	Cu metal

TABLE 2E. Primary opaque mineral phases in type 3.0 chondritic meteorites (Brearley and Jones 1998)

Name	Formula
Graphite	C
Kamacite	α-Fe,Ni metal
Taenite/Tetrataenite	γ-Ni,Fe metal
Awaruite	Ni_3Fe
Wairauite	Co,Fe,Ni metal
Copper	Cu metal
Troilite	FeS
Pyrrhotite	$Fe_{1-x}S$
Pentlandite	$(Ni,Fe)_9S_8$
Magnetite	Fe_3O_4
*Schreibersite	$(Fe,Ni)_3P$
*Perryite	$(Ni,Fe)_8(Si,P)_3$
*Oldhamite	CaS
*Sphalerite	ZnS
*Niningerite	(Mg,Fe,Mn)S
*Daubreelite	$FeCr_2S_4$
*Caswellsilverite	$NaCrS_2$
*Djerfisherite	$K_6Na(Fe,Cu,Ni)_{24}S_{26}Cl$
*Osbornite	TiN
*Cohenite	$(Fe,Ni,Co)_3C$

* Indicates highly reduced accessory phases in sulfide and metal nodules and clasts in enstatite chondrites.

amoeboid olivine aggregates (AOA), and other small (~1 mm diameter) refractory objects that formed in the high-temperature proto-stellar environment by evaporation, condensation, and melting of nebular materials.

Chondritic meteorites are complex aggregations of chondrules, CAI, AOA, and other refractory objects in a fine-grained matrix of mineral grains and dust. The least altered (type 3.0) chondritic meteorites—those that have experienced a minimum of aqueous and thermal alteration—range from extremely reduced EH3.0 enstatite chondrites to oxidized CV3.0 carbonaceous chondrites, and include CO3.0 and LL3.0 ordinary chondrites that formed under intermediate oxygen fugacities. Primary minerals are also largely preserved, although with some metamorphic overprint, in the relatively oxidized CK3 and R3 chondrites, as well as in EL3 enstatite chondrites and H3 and L3 ordinary chondrites. Chondrules and CAI, even those in the least-altered type 3.0 meteorites, have been subjected to complex histories of fluid interactions, multiple episodes of reheating, impacts and other events that have modified the initial mineralogy. Consequently, it is difficult to identify unambiguously "primary" chondrite minerals, which are defined as those earliest phases that formed directly through condensation, melt solidification, or solid-state recrystallization (MacPherson 2007). Nevertheless, type 3.0 chondrites are characterized by extreme mineralogical parsimony, as recorded in Tables 2b–2e (e.g., Brearley and Jones 1998; Ebel 2006; Messenger et al. 2006; MacPherson 2007).

The most important primary chondrule minerals (Table 2b) are Mg-rich olivine and pyroxene, with kamacite and taenite (both Fe-Ni metal) and troilite (FeS) as the major iron-bearing phases, and chromite ($FeCr_2O_4$) and pentlandite [$(Ni,Fe)_9S_8$] as important but volumetrically minor accessory minerals. Calcium-aluminum-rich inclusions feature a dozen primary Ca-Al-Mg oxide and silicate minerals, with at least 20 accessory minerals that usually occur as micro- or nano-scale phases (Table 2c). Additional mineralogical diversity occurs in the fine-grained predominantly silicate matrix of chondrites (Table 2d), and as opaque minerals, primarily metals and sulfides (Table 2e). Of special interest in this regard are phases in the remarkable enstatite chondrites, which display a distinctive mineralogy of highly reduced phases such as oldhamite (CaS), niningerite [(Mg,Fe,Mn)S], osbornite (TiN), caswellsilverite ($NaCrS_2$), perryite [$(Ni,Fe)_8(Si,P)_3$], and djerfisherite [$K_6(Fe,Cu,Ni)_{25}S_{26}Cl$].

All told, type 3 chondrites have been found to contain ~60 different primary minerals (Table 2), of which at least 20 occur only in micrometer- to nanometer-scale grains. These phases represent

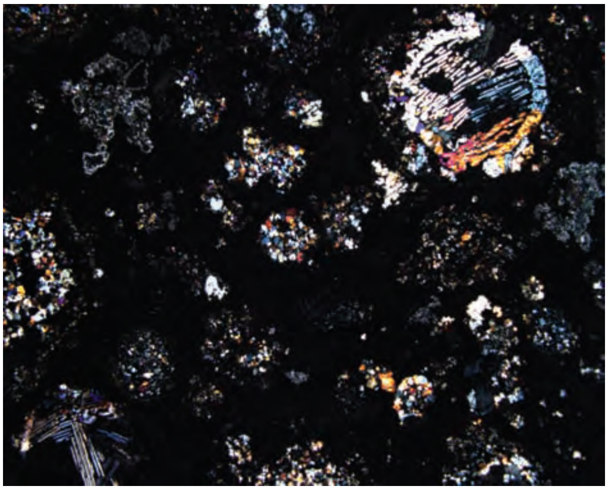

FIGURE 2. Photomicrograph of chondrules and calcium-aluminum-inclusions in the Allende (USNM 3658) CV3 carbonaceous chondrite, viewed in crossed Nichols (image width ~7 mm). Olivine is the most abundant birefringent mineral. These particles, along with the matrix in which they are contained, formed in the solar nebula and represent the chemical and mineralogical building blocks of planets. Photo courtesy of T. McCoy.

the earliest stage in the mineral evolution of terrestrial planets. It is important to recognize that unaltered chondrites contain all of the chemical complexity of terrestrial planets. Most of the 83 stable geochemical elements are present in solid solutions, but are presumably too widely dispersed to form their own discrete mineral phases. An intriguing question is the degree to which some of these elements may form additional nano-mineral domains within the meteorite matrix and at grain interfaces.

Stage 2. Aqueous alteration, metamorphism, and differentiation of planetesimals (4.56 to 4.55 Ga)

As planetesimal accretion progressed and chondrite parent bodies became larger, aqueous and thermal alteration led to new suites of minerals (Brearley and Jones 1998; Krot et al. 2006; Brearley 2006; MacPherson 2007). Low-temperature (typically <100 °C) aqueous alteration products of olivine and pyroxene (notably in CI-, CM-, and CR-type chondrites) include the first appearances of chlorite, serpentine, talc, and other phyllosilicate minerals (Brearley and Jones 1998), as well as hydroxides, sulfates, and carbonates. The effects of aqueous processes are dramatically illustrated by the occurrence of fluid inclusions in halite (NaCl), for example from the Monahans chondrite (Zolensky et al. 1999; Fig. 3).

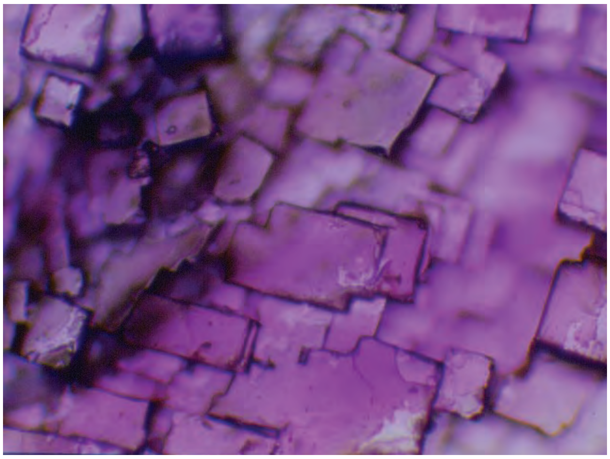

FIGURE 3. The Monahans chondrite has been found to contain halite crystals with fluid inclusions (image width ~5 mm), which point to extensive aqueous processing of the meteorite parent body (Zolensky et al. 1999). Photo courtesy of M. Zolensky and R. Bodner.

Thermal alteration below the (Fe,Ni)-FeS eutectic temperature (<950 °C; McCoy et al. 2006), including impact-induced alteration, yielded new species, notably the first significant appearance of albite, feldspathoids, and a variety of micas, amphiboles, and pyroxenes. Some chondrites also display the overprint of impact shock, which produced micrometer-scale grains of such unusual high-pressure phases as the majorite, akimotoite, and perovskite forms of $(Mg,Fe)SiO_3$, the wadsleyite and ringwoodite forms of $(Mg,Fe)_2SiO_4$, and the coesite and stishovite forms of SiO_2 (Chen et al. 1996; Sharp et al. 1997; Scott 2002; Xie et al. 2006). Yet, in spite of the appearance of these distinctive dense phases, the total known mineralogical repertoire of chondritic meteorites is limited to fewer than 150 different mineral species (Rubin 1997a, 1997b; Brearley and Jones 1998; Brearley 2006; MacPherson 2007).

Mineralogical diversity increased with the advent of planetesimal melting and differentiation, which was triggered in bodies greater than about 200 km in diameter principally by radiogenic heating from decay of ^{26}Al (Ghosh et al. 2006) and other short-lived radioisotopes (e.g., Shukolyukov and Lugmair 1992), although some authors continue to champion electrical conduction heating by the T-Tauri solar wind (Sonett et al. 1970) and impact heating (Lodders et al. 1993). The mineralogical diversity of achondrites results from differing extents of partial melting and differentiation, under the influence of variable oxygen fugacity, volatile contents, heat sources, and impact events (McCoy et al. 2006).

The most primitive achondrites, which appear to be derived from chondrites that experienced only partial melting and minimal differentiation, include acapulcoites, lodranites, and winonaites. These meteorites are composed principally of olivine, orthopyroxene (bronzite), plagioclase, troilite, and Fe-Ni metal. The presence of occasional relict chondrules, the lack of significant plagioclase in some of these (e.g., lodranites) compared to chondrites, and the occurrence of veins of metal and sulfide in some specimens point to partial melting (at T ranging from 950 to 1200 °C) and the removal of a plagioclase-rich melt (McCoy et al. 2006).

Planetesimals that underwent more extensive melting experienced large-scale separation of stony (crustal) and metallic (core) components, as well as fractionation of silicate magmas (Shukolyukov and Lugmair 2002; McCoy et al. 2006; Wadhwa et al. 2006). Individual differentiated meteorites, including several classes of stony achondrites as well as stony-iron and iron meteorites (Fig. 4), tend to be more equilibrated, and thus have fewer different mineral species, than many primitive chondrites (Weisberg et al. 2006). Nevertheless, a great variety of differentiated meteorites evolved and many minerals appeared for the first time in these achondrites.

Several distinctive types of stony achondrites represent planetesimal crust. Eucrites, the most common achondrites with an igneous mineralogy dominated by plagioclase and pyroxene, are similar to terrestrial basalts and thus represent partial melts. Eucrites feature the first significant appearance of several important rock-forming minerals, including the quartz form of SiO_2, potassium feldspar ($KAlSi_3O_8$), titanite ($CaTiSiO_5$), and zircon ($ZrSiO_4$). Diogenites, by contrast, are Ca- and Fe-poor meteorites that formed through melting and accumulation of orthopyroxene, while brachinites represent olivine cumulates. Superimposed on these lithologies in many meteorites are effects of impacts, brecciation, hydrothermal alteration, and other metamorphism.

Iron-nickel meteorites, which represent the core material of differentiated planetesimals, are dominated by Fe-Ni alloys (kamacite, taenite), with significant metal sulfides (troilite, daubreelite), carbides (cohenite and haxonite), graphite, and the phosphides barringerite [$(Fe,Ni)_2P$] and schreibersite [$(Fe,Ni)_3P$], which may have provided Earth with a major prebiotic source of reactive phosphorus (Pasek et al. 2007). Iron-nickel meteorites tend to be relatively simple in their major mineralogy, but they incorporate a host of exotic transition metal sulfide minerals, as well as more than two dozen novel phosphates, including the graftonite and sarcopside forms of [$(Fe,Mn)_3(PO_4)_2$], buchwaldite ($NaCaPO_4$), farringtonite [$Mg_3(PO_4)_2$], and the Na-Ca-Mg phosphates johnsomervillite, panthite, chladniite, and brianite (Rubin 1997a, 1997b). Other important accessory minerals include such high-pressure phases as the coesite, stishovite, and post-stishovite forms of SiO_2, and diamond and its closely related carbon polymorph, lonsdaleite.

A total of ~250 mineral species are known to occur in all types of meteorites (e.g., Mason 1967; Rubin 1997a, 1997b; Brearley and Jones 1998; Gaffey et al. 2002; MacPherson 2007). All varieties of meteorites have fallen throughout Earth's 4.5 billion year history; hence, all of these diverse meteorite minerals, including many phases that are thermodynamically unstable at surface conditions, have been present continuously in Earth's near-surface environment, albeit in small quantities. These minerals, dominated volumetrically by magnesium silicates, iron sulfide, and Fe-Ni metal, provided raw materials for the accreting Earth and other terrestrial planets.

FIGURE 4. The Staunton iron meteorite (USNM 590), ~20 cm in length. This polished and etched slice displays the distinctive Widmanstatten pattern characteristic of many iron meteorites, with plates of low-Ni kamacite (Fe,Ni metal) exsolved from high-Ni taenite at cooling rates of 1–100 °C/Myr. Iron meteorites sample the cores of differentiated asteroids, provide some of our best clues to the chemical nature of our own core, and continue to fall to Earth. Photo courtesy of T. McCoy.

THE ERA OF CRUST AND MANTLE REWORKING (4.55 TO 2.5 GA)

Earth's crust and outer mantle were violently disrupted and largely melted (and thus "reset") by the epic Moon-forming impact event at ~4.55 Ga (Tonks and Melosh 1993; Ruzicka et al. 1999; Touboul et al. 2007). At that early stage, virtually all near-surface mineralogical diversity of the four terrestrial planets and Earth's Moon developed by crystallization of igneous rocks, supplemented by a steady bombardment of asteroidal and cometary material. Nevertheless, Earth's mineralogy was poised to diversify as a result of intense crust and mantle reworking.

The major challenge to documenting Earth's mineral evolution prior to the Neoarchean Era (~2.8 Ga) is the relative paucity and typical extreme alteration of the rock record. No known rocks survive from before ~4.03 Ga, though hope may be held out that relatively unaltered early Hadean samples might eventually be recovered in the form of Earth meteorites on the Moon (Armstrong et al. 2002; Chapman 2002; Jakosky et al. 2004). Consequently, many critical aspects of early Earth geology and petrology—the timing of the initiation of subduction and orogenic processes, the chronology of the formation of cratons and the first continents, and the identities and distribution of major lithologies, for example—represent topics of debate and contention. It is not our intention to resolve these debates, nor is the exact timing of such events critical to the general concept of mineral evolution. Whatever the chronology, many of Earth's earliest mineral-forming processes can be inferred from the existing rock record and knowledge of petrologic, geochemical, and geodynamic principles.

Stage 3. Initiation of igneous rock evolution (4.55 to 4.0 Ga)

Igneous activity appears likely to have dominated Earth's near-surface mineral evolution for at least half a billion years following planetary accretion, differentiation, and formation of primary magmas. The earliest shallow crustal igneous rocks would have been mafic and ultramafic lithologies, notably basalts composed primarily of plagioclase, pyroxene, some olivine and minor oxides, and similar in composition to eucrites. Slow crystallization of magma bodies would have resulted in crystal settling and cumulates, for example in extensive layers of chromite (Kerrich et al. 2005). Very large magma bodies, or magma oceans, may also have formed low-density plagioclase-rich crusts by flotation, as observed for the ancient anorthositic crust of the lunar highlands.

The oldest known tangible pieces of evidence of Hadean mineralogy are detrital zircon grains, with ages of 4.4 to 4.0 Ga, which have been recovered from Archean quartzites from Western Australia (Fig. 5). These ancient mineral grains have been interpreted variously as remnants of early granitic continental crust (Harrison et al. 2005; Cavosie 2005; Cavosie et al. 2005, 2006) or pre-continental mafic to ultramafic crust (Shirey et al. 2008). Shirey et al. (2008) employed Lu-Hf isotopic data to suggest that the Hadean Earth's wet mafic igneous veneer was repeatedly cycled by fractional melting, fractional crystallization, and magma immiscibility—processes that would have led to a diversity of igneous lithologies, in part following Bowen's familiar reaction series (Bowen 1928). The reaction series is characterized by two independent, but contemporaneous, mineralogical trends: plagioclase feldspars display a continuous variation from Ca-rich (anorthitic) to Na-rich (albitic) compositions, and subsequently to Na- + K-rich alkali feldspars, whereas ferromagnesian minerals form a discontinuous series from Mg-olivine to increasingly iron-rich pyroxenes and, following buildup of H_2O in the residual magma, hornblende, and ultimately biotite. These parallel mineral progressions lead to a range of igneous lithologies—gabbro, diorite, granodiorite, and granite—though variations in temperature, pressure, magma composition, and magma chamber geometry, for example, result in a wide variety of bulk rock compositions. This wider spectrum of bulk compositions allowed for a greater diversity in mineralogy (e.g., Yoder 1976; Hess 1989; Marsh 2006).

These igneous events represent the probable end point of mineral evolution for relatively small (<5000 km diameter), volatile-poor terrestrial bodies, including the Moon (Jolliff et al. 2006), Mercury (Clark 2007), and asteroid 4Vesta, from which the eucrites are thought to derive (Binzel and Xu 1993). With the exception of space weathering caused by the action of cosmic rays, effects of solar wind particles, and bombardment by micrometeorites (Hapke 2001), the near-surface mineralogy of such objects is essentially frozen. The limited near-surface mineralogical diversity of these bodies, which we estimate to be no more than ~350 species, points to the dominant role that volatiles play in the mineral evolution of larger terrestrial planets.

Igneous activity on the volatile-rich Earth (as well as on Venus and Mars) commenced immediately after initial accretion at ~4.55 Ga and led to new near-surface mineralogical diversity. Much of that diversification resulted from volcanic outgassing and fluid-rock interactions associated with the formation of the atmosphere and hydrosphere. Earth's principal initial atmospheric components are thought to have been N_2, CO_2, and H_2O, with minor H_2S (e.g., Holland 1984), though a more reduced suite of volcanic gases, including CO, H_2, and CH_4, also has been suggested as important localized atmospheric inputs during the Hadean Eon (Kump et al. 2001; Catling and Claire 2005). An immediate mineralogical consequence of these interactions would have been copious formation of hydrous silicates and hydroxides, including serpentinization and the first significant production of clay minerals. In addition, as Earth's poles cooled below the freezing point, crystalline H_2O would have appeared for the first time.

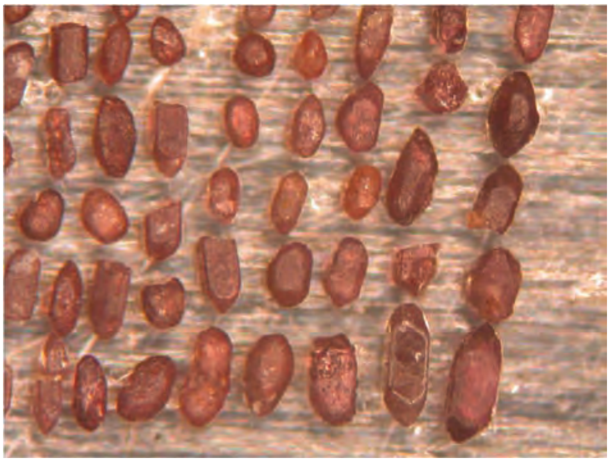

FIGURE 5. Detrital zircon grains (maximum grain dimension ~200 μm) with ages of 4.4 to 4.0 Ga have been recovered from Archean quartzites from Western Australia and are interpreted as remnants of early granitic continental crust or pre-continental mafic to ultramafic crust (Cavosie 2005; Cavosie et al. 2006). Photo courtesy of J. Valley.

From their inception at least 4.3 billion years ago (Mojzsis et al. 2001), oceans would have steadily increased in salinity [predominantly Na, Ca, Mg, and Cl, though ratios may have varied significantly over time (e.g., Hardie 1996, 2003; Lowenstein et al. 2001; Dickson 2002)]. Ocean concentrations of sulfate would also have increased slightly by photolytic and lightning-induced reactions in the atmosphere and subsequent ocean-atmosphere exchange. Oceanic nitrate levels probably remained minimal because of the low efficiency of nitrate-producing reactions in anoxic conditions, as well as facile deep-ocean hydrothermal conversion of nitrate to ammonia (Brandes et al. 1998). These compositional changes may have resulted in Earth's first evaporite deposits with their associated sulfate minerals, although no traces of ephemeral evaporite minerals have been found prior to about 3.4 Ga (Tice and Lowe 2004).

An important consequence of volcanic degassing was the gradual chemical decoupling of the crust and shallow mantle from the deep interior (Rohrbach et al. 2007; Burgisser and Scaillet 2007). Photo-dissociation of water and subsequent hydrogen loss may have contributed to the oxidation of the crust relative to the mantle. For a time early in Earth's history, the oxidation state of the surface may have been buffered, at least in part, by the mantle through the mediating effects of reduced volcanic gases (Kump et al. 2001). Nevertheless, mantle oxygen fugacity (and hence the composition of its volcanogenic gases) had approached its modern value by 3.9 Ga, based on Cr and V trace concentrations in peridotites and komatiites (Canil 1997, 2002), as well as Fe^{3+}/Fe^{2+} in Cr-spinels (Delano 2001). Thus, the mantle and crust must have begun to chemically decouple relatively early in Earth's history.

Given the present day atmospheres on Venus and Mars, as well as chemical, mineralogical, and morphological evidence for once extensive surface water on Mars (Squyres et al. 2004; Paige 2005; Bibring et al. 2006; Andrews-Hanna et al. 2007), we can be reasonably certain that these planets progressed to this stage in their mineral evolution. However, as yet there is no positive evidence that Venus and Mars experienced three additional key steps to further mineral diversification: (1) production of extensive granite (and its volcanic equivalent rhyolite); (2) development of chemically evolved and aerially extensive continental crust and lithosphere (whether or not this crust displayed the long-term stability of a craton); and (3) plate tectonics. Without these processes, and the consequent extensive hydrothermal and tectonic-magmatic reworking of a planet's outer several tens of kilometers, it is unlikely that a planet can develop more than a few hundred near-surface mineral species (see, for example, Campbell and Taylor 1983).

Stage 4. Granitoid production and the initiation of craton formation (~4.0 to 3.5 Ga)

Archean cratons are relatively stable but lithologically complex fragments of ancient crust and co-evolved subcontinental mantle lithosphere (Bleeker 2003; Pearson 1999; Smithies et al. 2005a). Although a large proportion of cratonic crust is Neoarchean in age, and a majority of cratons only attained final stability after 2.7 Ga, nearly all contain ancient nuclei with a rock record that stretches back to >>3.5 Ga. Hence, the initiation of craton formation can be traced back to at least the earliest Archean and possibly earlier (Fig. 6). Two important and intimately related processes contributed to the formation and eventual stabilization of Archean cratons: (1) continued granitoid production and growth of buoyant lithosphere, thus increasing the scale and preservation potential of early crust, and (2) continued internal differentiation, with irreversible transport of heat-producing elements to the upper crust, and resulting cooling and strengthening of the crustal (lithospheric) profile (Sandiford and McLaren 2002; Jordan 1978). Both processes were to some extent stochastic: only those ancient crustal nuclei that became embedded in and surrounded by younger buoyant lithosphere survived with their coupled subcontinental lithospheric mantle root. Only those early landmasses that grew to sufficient size, internally differentiating in the process and restricting deformation to their margins, acquired the strength ("kratos" in ancient Greek) to develop long-term stability. The early geological record thus has an aspect of "survival of the fittest" (Bleeker 2002).

Whatever the exact timing, production of abundant granitoid rocks, initial craton development, and the assembly of the first micro-continents represent key innovations in the mineral evolution of a terrestrial planet. Eutectic-like or minimum melting of mafic and ultramafic lithologies resulted in suites of granitoid rocks, from tonalite-trondhjemite-granodiorite (TTG) to granodiorite-granite-monzogranite (GGM) and high-K syenite-granite (SG) suites (Zegers 2004). On Earth the more Na-rich TTG suites dominated the earliest stages of continent formation, while GGM and SG suites appear to have arisen subsequently, primarily through secondary partial melting of older TTGs (Smithies and Champion 2000; Smithies et al. 2003).

The composition of granitoids closely corresponds to eutectic melting in the SiO_2-Al_2O_3-Na_2O-K_2O system, and as such granites can occur in a variety of lithologic and tectonic settings. For example, granitic magmas occur as the last stage in the liquid line of descent of oceanic and continental basalts (Perfit et al. 1980). However, this highly fractionated, silica-rich residual liquid represents only a few percent of the basaltic parent magma, so it is unlikely that this widely dispersed and highly viscous residual magma could accumulate to form significant intrusive bodies as the result of basalt crystallization alone (Hersum et al. 2005). It is also important to note that granite cannot be derived directly from melting of a peridotitic mantle source because granitic magmas are not in equilibrium with Mg-rich olivines. Therefore, most granitoid rocks must be derived from other sources.

The principal mode of granite petrogenesis is thought to be magmas produced by partial melting of wet igneous and siliciclastic sedimentary rocks (e.g., White and Chappell 1983; Hess 1989; Kemp et al. 2007; Eiler 2007). Eutectic melting of peraluminous sediments, for example, can yield up to 25% granitic melt, with melting commencing at temperatures as low as 630 °C at 1 GPa and 670 °C at 0.3 GPa (Luth et al. 1964). Similarly, granitic magmas form from partial melting of basalt or andesite under high H_2O pressure. Heat provided by successive, episodic intrusions of basalt into the base of the crust can thus repeatedly generate significant amounts of granitoid rocks in the overlying continental crust (Parman 2007; Pearson et al. 2007).

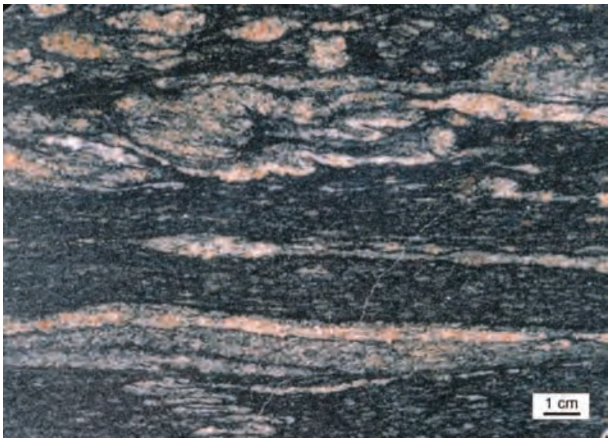

FIGURE 6. The 4.03 Ga Acasta Gneiss from the Slave Craton, northwestern Canada, the oldest known rock unit on Earth, is crosscut by 3.6 Ga granite veins. Photo by W. Bleeker.

The timing of the appearance of Earth's first granitoid rocks is uncertain; however, the partial melting mechanism invoked for most such bodies implies that significant granitoid formation could not have occurred prior to the initial assembly of basaltic crust, and perhaps the accumulation of significant sediment wedges as well. Bédard (2006) has suggested that TTG granitoid formation first occurred prior to plate tectonics and may have been triggered by mantle plumes, which partially melted basaltic crust. Zircon from Archean sediments of Jack Hills, Australia, dated at 4.38 Ga has been interpreted as an indication that production of granitic continental crust material was active within 150 million years of accretion. Evidence includes $\delta^{18}O$ values higher than mantle values (Wilde et al. 2001; Mojzsis et al. 2001; Cavosie et al. 2005; Harrison et al. 2005; Valley et al. 2006; Kemp et al. 2006, 2007; Scherer et al. 2007; Trail et al. 2007), as well as K-feldspar and monazite inclusions in some of these ancient zircons (Maas et al. 1991, 1992; Cavosie et al. 2004; Crowley et al. 2005). However, these postulated early granitic masses, possibly because of their limited scale, were likely recycled into the mantle prior to the end of the Hadean Eon and thus are not preserved (Shirey et al. 2008).

Even if stable continent formation required an additional 600 million years (Boyet et al. 2003; Rino et al. 2004), many granitic minerals, including quartz (SiO_2), K-feldspar ($KAlSi_3O_8$), albitic plagioclase ($NaAlSi_3O_8$), and a variety of micas, amphiboles, and alkali pyroxenes, would have appeared in the Hadean Eon for the first time in significant amounts. Peraluminous granites, derived from partial melting of Al-rich shales, also feature muscovite [$KAl_2(AlSi_3)O_{10}(OH)_2$], cordierite ($Mg_2Al_4Si_5O_{18}$), and the sillimanite and andalusite forms of Al_2SiO_5 (depending on the temperature and pressure of crystallization), while peralkaline granites often contain the alkali silicates acmite ($NaFeSi_2O_6$)

and riebeckite [$Na_2(Fe,Mg)_5Si_8O_{22}(OH)_2$]. The common granite accessory phases, such as titanite ($CaTiSiO_5$), zircon ($ZrSiO_4$), monazite [$(Ce,La,Y,Th)PO_4$], apatite [$Ca_5(PO_4)_3(OH,F)$], and fluorite (CaF_2), would also have been produced in significantly greater abundance than previously.

The nature of early cratonic crust constitutes an important contrast between the Archean Earth and that of today. The low-relief basaltic (pre-granite) surface of the prebiotic Earth was likely subject to weathering by hydration and intense mechanical erosion (Dott 2003), including a tidal cycle of <8 h and much greater amplitude (Lathe 2006; Varga et al. 2006). With no plants to hold regolith, physical erosion may have prevented extensive soil formation, and might have led to significant near-shore sediment wedges. If the original protolith for the Jack Hills zircon was a clay-rich marine sedimentary rock, then an active sedimentary cycle must also have been established within Earth's first 150 million years.

An important mineralogical consequence of GGM suites of granites was the enrichment of more than 20 rare pegmatophile elements in residual supercritical aqueous fluids and the eventual production of pegmatite minerals (Foord 1982; Moore 1982; Černý 1982a; Ewing and Chakoumakos 1982; London 1987, 2008). Development of complex pegmatites marked the first occurrences of distinctive minerals of lithium (spodumene, lepidolite, cookeite, triphyllite), cesium (pollucite), boron (tourmaline, datolite, axinite, danburite), beryllium (beryl, bertrandite, gadolinite, phenakite, bromellite), and Nb-Ta (pyrochlore, columbite, tantalite), as well as a host of Zr-Hf, Ga, Sn, rare-earth elements, and U minerals. Pegmatites feature >550 minerals, many of which are unique to those environments. Furthermore, the development of giant single crystals (>1 m in length) of Li-, Be-, B-, Cs-, and other rare element-containing minerals underscores the repeated melting, fluid cycling, and unusual elemental concentration that occurred in some of these bodies (Černý 1982b).

Consider one of the oldest known complex pegmatites, the 2.67 Ga Tanco pegmatite from Manitoba. Based on the chemistry of Cs, London (2008) estimates that this relatively small body represents at a minimum the extraction and concentration of 5% melt from 18 000 km^3 of metapelite (assuming 100% of that melt coalesced to form the pegmatite, rather than becoming widely dispersed in mineral interstices). Accordingly, complex pegmatites represent multiple cycles of large-scale eutectic melting, aqueous phase concentration, and consequent extreme elemental concentration, and thus must considerably postdate the first GGM granite suites.

Granite formation may represent the end point of igneous mineral evolution for some terrestrial planets. On Earth, however, plate tectonics coupled with dramatic changes in ocean and atmospheric chemistry led to significant additional stages of mineral diversification.

Stage 5. Plate tectonics and large-scale hydrothermal reworking of the crust (>>3.0 Ga)

The timing of the beginnings of plate tectonics, and in particular the commencement of large-scale subduction and associated crustal reworking and arc volcanism, remains a matter of intense debate (Stern 2005; Cawood et al. 2006). Nevertheless, most researchers conclude that at least some form of episodic subduction was active significantly before 3.0 Ga, and possibly before 4.0 Ga (Harrison et al. 2005; Smithies et al. 2005b; Witze 2006; Silver et al. 2006; Silver and Behm 2008).

Shirey et al. (2008) present several lines of evidence regarding the early stages of lateral tectonics. Separation of the primordial magma ocean and silicate perovskite was active >3.5 Ga; hence some form of mantle convection was operational at that early stage. Pillow basalts and sheeted dikes from the ~3.8 Ga Isua supracrustal belt, southwest Greenland (Komiya et al. 1999; Furnes et al. 2007) suggest at least localized seafloor spreading (Fig. 7), while the formation of supracrustal belts in Archean cratons (>3 Ga) and Os isotopic evidence from 3.5 Ga diamonds point to subduction prior to 3 Ga. Shirey et al. (2008) thus suggest that initial stages of plate tectonics had begun by ~3.85 Ga. Further, they argue that prior to plate tectonics the crust was predominantly mafic (not granitic), and that significant continent building and granite formation postdated lateral tectonics, even if divergent boundaries and subduction zones had not yet become established on a global scale. Accordingly, Workman and Hart (2005) suggest a ~3 Ga age for modern continental crust formation.

Whatever the timing of its onset, lateral tectonics, large-scale recycling of ocean lithosphere, and convection (if not plate tectonics sensu stricto) had significant mineralogical consequences (Parnell 2004). Most notably, extensive hydrothermal processing of the upper mantle and crust associated with magmatic and volcanogenic processes at subduction zones and at ridges produced the first episodes of massive sulfide deposition and associated precious metal concentrations (Sangster 1972; Hutchinson 1973). Many hydrothermal ore deposits arise from interactions with hot solutions (initially >600 °C) ascending through a volume of rock that may exceed 30 km^3 (Barnes and Rose 1998). Chemical complexation in these solutions, principally with Cl^-, selectively dissolves and concentrates many incompatible elements, including the transition metals that provide the principal economic rationale for exploitation. Ore body precipitation may occur at relatively shallow depths through a combination of cooling, pressure release, fluid mixing, and fluid-rock interactions (Robb

FIGURE 7. Pillow basalts from the 3.8 Ga Isua supracrustal belt, southwest Greenland suggest at least localized seafloor spreading. Photo by D. Papineau.

2004), as well as near-surface microbial activity (Labrenz et al. 2000; Edwards et al. 2003; Reith et al. 2006).

The earliest evidence for hydrothermal ore deposits may be volcanic-hosted massive sulfide and stratiform Cu-Zn-Pb sulfide deposits in the North Pilbara Terrain of Western Australia, which have been dated at ~3.5 Ga, based on the age of felsic volcanic host rocks. In addition, Cu-Mo porphyry deposits associated with felsic plutons in the North Pilbara have been dated at ~3.3 to 3.4 Ga, based on direct U-Pb dating of titanite and zircon (Huston et al. 2002). The important 2.9 to 2.7 Ga detrital gold and uranium deposits of the Witwatersrand, as well as the 2.4 Ga Blind River uranium deposits of Canada, which must have been derived from erosion of earlier ore bodies, also provide evidence for mechanisms that produced Archean hydrothermal ores (Meyer 1985; Kerrich et al. 2005). For the Witwatersrand gold, Kirk et al. (2002) determined Re-Os isochron ages just over 3.0 Ga. Deep-seated hydrothermal ore-forming processes were thus active prior to 3.0 Ga and are contemporaneous with significant craton formation and assembly (Folinsbee 1982; Bleeker 2003).

Less than two dozen different minerals account for much of the economic production in massive sulfide deposits, but the mineralogical diversity of these bodies is much greater because of a rich spectrum of associated minor phases including selenides, tellurides, arsenides, antimonides, and a host of sulfosalts. Dana (1958) records more than 125 such minerals, compared to 37 sulfides (of which fewer than 20 species account for the principal ore minerals). Additional new mineral phases, including many sulfosalts and complex sulfides, form during the inevitable metamorphism of sulfide deposits.

Another mineralogical consequence of plate tectonics was the uplift and subsequent exposure of regional metamorphic terrains—events that could have brought characteristic moderate-pressure phases such as kyanite (Al_2SiO_5), lawsonite ($CaAl_2Si_2O_8·2H_2O$), glaucophane [$Na_2(Fe,Mg,Mn)_3Al_2Si_8O_{22}(OH)_2$], chloritoid [$(Fe,Mg)_2A_{14}Si_2O_{10}(OH)_4$], staurolite [$(Fe,Mg)_2Al_9(Si,Al)_4O_{20}(O,OH)_4$], and jadeite ($NaAlSi_2O_6$) to near-surface environments.

Stage 6. The anoxic biosphere of the Archean Eon (3.9 to 2.5 Ga)

The Archean Eon saw the rise of microbial life, yet the influence of life on Earth's mineral diversity was minimal prior to the Proterozoic Eon. Banded iron formations (BIFs) are among the earliest types of sedimentary rocks found in Eoarchean supracrustal belts and represent a major economic source of iron ore (Fig. 8). The abundance of BIFs during the Precambrian is uneven with a few occurrences in the Eo- and Paleoarchean Eras (perhaps corresponding to the paucity of the early rock record) and a culminating development near the Archean-Proterozoic boundary (Isley and Abbott 1999; Klein 2005). The origin of these chemically precipitated sedimentary rocks is not well understood, but the early hypothesis that microorganisms were responsible for their formation (e.g., LaBerge 1973) has recently received support from experimental work showing that rates of photooxidation of Fe^{2+} and Mn^{2+} are negligible when compared to rates of biological oxidation (Anbar and Holland 1992; Konhauser et al. 2007a). The hypothesis that BIF precipitation requires either the presence of photosynthetically produced O_2 or Fe^{2+}-oxidizing microorganisms (Cloud 1972; Holland 1973; Widdel et al. 1993; Akai et al. 1999; Tazaki 2000; Konhauser et al. 2002; Kappler et al. 2005) is significant because BIFs are one of the oldest types of sedimentary rocks. However, BIFs are not unambiguously biotic (Klein 2005). Significant abiotic components of BIFs originated from hydrothermal sources as evidenced by REE abundances, which show that Fe^{2+}, Mn^{2+}, and some SiO_2 were derived from such fluids (Jacobsen and Pimentel-Klose 1988; Bau and Möller 1993; Klein 2005). In contrast, the Ge/Si ratios of chert bands in BIFs suggest that some of the silica was derived from weathering of continental material and thus suggests different sources (hydrothermal and continental) for different BIF components (Hamade et al. 2003).

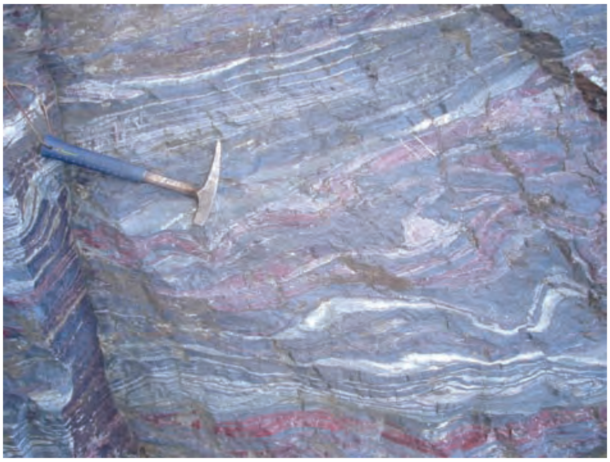

FIGURE 8. Banded iron formations from the ~2.76 Ga Temagami greenstone belt of Ontario, Canada, are dominated by magnetite, chert, and jasper and are typical of Neoarchean BIFs. Photo by D. Papineau.

As inferred from studies of low-grade metamorphosed exposures, Precambrian BIFs initially formed from colloidal/gel SiO_2 and aqueous Fe^{2+} and Fe^{3+} in environments with variable amounts of dissolved Na^+, K^+, HCO_3^-, Mg^{2+}, and Ca^{2+} in porewater (Klein 1974). Environmental and compositional factors that influence redox state and pH dictate the composition of BIFs, which informally can be classified into three families based on their dominant mineralogy: an oxide facies [with jasper, hematite (Fe_2O_3), and/or magnetite (Fe_3O_4)], a sulfide facies [often organic-rich and containing pyrite and marcasite (both FeS_2), pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$)], and a carbonate facies {including siderite ($FeCO_3$), ankerite [$FeCa(CO_3)_2$], Fe-dolomite [$Ca(Mg,Fe)CO_3$], and calcite ($CaCO_3$)}. The most abundant BIF type in the Archean is the oxide facies, but sulfide and carbonate facies also occur. The mineralogy of Eoarchean BIFs, such as those from the Isua supracrustal belt in southwest Greenland and in the Nuvvuagittuq supracrustal belt in northern Quebec, is typically dominated by quartz and magnetite (Dymek and Klein 1988; Dauphas et al. 2007). Starting in the Paleoarchean Era, hematite and jasper are also found in some BIFs, such as in the 3.25 Ga Fig Tree Group of the Barberton Greenstone Belt in South Africa. The mineralogy of BIFs can be significantly transformed during post-depositional processes of diagenesis, metamorphism, and metasomatism. Upon diagenesis, the ferruginous-siliceous gel crystallized into chert, hematite, hydromagnetite ($Fe_3O_4·nH_2O$, which eventually transformed to magnetite), amorphous greenalite [$Fe_{2+x}Si_2O_5(OH)_4$], stilpnomelane [$K(Fe,Mg)_8(Si,Al)_{12}(O,OH)_{27}·nH_2O$], and fine-grained carbonate mixtures. Subsequent metamorphic recrystallization led to variable mineral assemblages that can include chlorite [$(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$], cummingtonite-grunerite amphiboles [$(Mg,Fe)_7Si_8O_{22}(OH)_2$], minnesotaite [$(Mg,Fe)_3Si_4O_{10}(OH)_2$], chamosite [$(Fe,Mg)_5Al_2Si_3O_{10}(OH,O)_8$], almandine ($Fe_3Al_2Si_3O_{12}$), orthopyroxene [$(Mg,Fe)SiO_3$] and clinopyroxene [$Ca(Mg,Fe)SiO_3$], hornblende [$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$], fayalite ($Fe_2SiO_4$), and pyrrhotite (Klein 2005).

The advent of oxygenic photosynthesis and the oxygenation of Earth's atmosphere are of central concern in the coevolution of minerals and life. Even without biological O_2 sources, the atmosphere may have experienced a gradual, but minor, oxidation through photodissociation of water and subsequent hydrogen escape (Walker 1977; Holland 1984; but see Tian et al. 2005, who argue for significant concentrations of atmospheric H_2). Serpentinization and microbial production of atmospheric methane (which also leads to hydrogen escape) would also have contributed to gradual atmospheric oxidation (Rye et al. 1995; Rye and Holland 1998; Catling et al. 2001; Pavlov et al. 2003). Even so, microbial photosynthesis became the dominant oxygen-producing mechanism sometime in the Archean Eon (Brocks et al. 1999; Rosing and Frei 2004). While the oldest unambiguous fossils of photosynthetic organisms are from the ~1.9 Ga Gunflint black cherts from northwest Ontario (Barghoorn and Tyler 1965; Knoll 2003a), several researchers argue for evidence of photosynthetic processes much earlier in the Eo- and Paleoarchean rock record (Schopf and Packer 1987; Schidlowski 1988; Schopf 1993; Rosing 1999; Summons et al. 1999; Brocks et al. 2003; Noffke et al. 2003; Tice and Lowe 2004; see, however, Brasier et al. 2002).

In spite of these potential oxygen sources, mineralogical and isotopic evidence indicates that Earth's atmosphere was mostly devoid of free oxygen prior to 2.25 Ga (Holland 1984; Farquhar et al. 2001). The occurrence of rounded detrital grains of pyrite (FeS_2), siderite ($FeCO_3$), and uraninite (UO_2) in the South African Witwatersrand and Canadian Blind River Archean deposits suggests erosion and transport in an oxygen-deficient environment (Rasmussen and Buick 1999; England et al. 2002). The lack of a cerium anomaly in the 2.5 Ga Pronto paleosols (Murakami et al. 2001) and the general absence of iron hydroxides in paleosols older than 2.3 Ga (Holland and Rye 1997) provide further mineralogical evidence for an essentially oxygen-free atmosphere prior to the Paleoproterozoic (see, however, Ohmoto 1997 for a dissenting viewpoint). Multiple sulfur isotope ratios in sedimentary rocks indicate that the atmosphere was mostly anoxic from the beginning of the sedimentary rock record at about 3.85 Ga until the Paleoproterozoic glaciations (Farquhar et al. 2000, 2001, 2007; Mojzsis et al. 2003; Ono et al. 2003; Bekker et al. 2004; Papineau et al. 2005, 2007; Papineau and Mojzsis 2006). It should be noted that even if the Mesoarchean atmosphere was lacking in oxygen, the possibility remains of "oxygen oases" in which oxygen-producing cyanobacteria locally influenced the mineralogy of redox-stratified marine environments. However, while small amounts of oxygen may have occurred locally, it did not accumulate globally (Ono et al. 2006; Ohmoto et al. 2006; Kaufman et al. 2007; Farquhar et al. 2007). This lack of oxygen may be due to higher levels of reducing gases and oxygen sinks in the Archean atmosphere promoted by predominantly submarine volcanism (Kump and Barley 2007).

Even in the absence of free oxygen, microbial activity could have triggered significant mineralogical consequences. For example, Rosing et al. (2006) have proposed that plate tectonics and biological activity in the early Archean may have had a significant effect on the rate of granite production, and hence the stabilization of continents prior to 3.0 Ga. Their argument rests on the fact that granite formation is largely a consequence of the subduction and dehydration of altered basalt and sediments. Microbial activity is known to increase rates of silicate weathering by an order of magnitude over abiotic processes (Bennett et al. 1996; Paris et al. 1996; Barker et al. 1998; Tazaki 2005). It is possible, therefore, that surface microbial communities on an anoxic world may have affected the rate of continent formation.

One of the most dramatic mineralogical innovations of the Mesoarchean Era (3.2–2.8 Ga) was the first precipitation of massive carbonate sequences in relatively shallow epicontinental environments. The history of carbonate deposition on Earth is, in part, a history of atmospheric CO_2 concentration, and several lines of evidence suggest that atmospheric CO_2 levels may have been much higher and fluctuated more significantly on the early Earth. Sagan and Chyba (1997) pointed to the need for significant concentrations of some greenhouse gases, presumably some combination of CO_2, water vapor, and methane, throughout much of Earth's first 2 billion years because of the so-called "early faint Sun paradox." The Sun's luminosity has increased gradually over geologic time, from about 70% of present intensity 4.5 billion years ago, to roughly 90% 1.5 billion years ago (Bahcall et al. 2001). Without significant greenhouse warming, the early Earth would have been frozen, and thus CO_2 appears to have been a significant greenhouse gas throughout the Paleo- and Mesoarchean Eras. Rye et al. (1995) place CO_2 concentrations at 2.75 Ga at ~100× present levels based on observations of Archean paleosols, while Kaufman and Xiao (2003) used microfossil isotope data to estimate that the atmospheric pressure of CO_2 at 1.4 Ga was at least 10 and perhaps as much as 200× greater than today. The occurrence of calcified cyanobacteria in 1.2 Ga dolostones has been interpreted to indicate CO_2 levels <0.36%, ~10× current levels (Kah and Riding 2007). Others have proposed Precambrian CO_2 levels at least 1000× that of today (Walker et al. 1981; Ohmoto et al. 2004).

Carbonates are present throughout the geologic record, but their abundances and mineralogy changed significantly over time (Sumner 1997). The earliest known carbonates are iron-bearing ankerite [$Ca(Fe,Mg)(CO_3)_2$] and siderite ($FeCO_3$) from calc-silicate rocks in the >3.77 Ga Isua supracrustal belt, which have been interpreted as metasomatic in origin (Rose et al. 1996). Ferruginous carbonate minerals are also common as accessory phases in BIFs from Isua and these are likely not metasomatic (Dymek and Klein 1988). In the >3.75 Ga Nuvvuagittuq supracrustal belt in northern Québec, ferruginous carbonates in sedimentary rocks have been proposed to have formed from the alteration of primary siderite on the basis of fractionated Fe isotopes, which would also imply deposition under high p_{CO_2}

(Dauphas et al. 2007). Ferroan carbonates, which form massive deposits hundreds to thousands of square kilometers in aerial extent in beds tens to hundreds of meters thick (Kimberley 1989), cannot precipitate without restrictive chemical conditions. These conditions include (1) aqueous Fe^{2+}; (2) anoxic ocean water to prevent iron removal by FeO(OH) precipitation; (3) low SO_4^{2-} and H_2S to prevent iron removal by pyrite (FeS_2) precipitation; and (4) significant dissolved HCO_3^- (Moore et al. 1992; Ohmoto et al. 2004).

An ongoing debate centers on the absence of siderite ($FeCO_3$) in Archean paleosols, which are contemporaneous with marine ferroan carbonate precipitation. Rye et al. (1995) cite this absence as evidence that atmospheric CO_2 was not the major greenhouse gas at that time. Ohmoto and coworkers (2004), by contrast, explain the absence of siderite in paleosols as a consequence of trace levels of atmospheric O_2, which precluded surface formation of siderite, even with high CO_2 concentrations.

An important unanswered question regarding Eo- and Paleoarchean mineralogy is the extent to which biological activity, either directly or indirectly, influenced mineral deposition. Unequivocal biomineralization did occur on a limited scale in the Paleoarchean Era, however. Stromatolites are laminated carbonate or cherty structures dating from at least 3.48 Ga (Walter et al. 1980; Lowe 1980; Buick et al. 1981; Byerly et al. 1986; Walter 1994; Grotzinger and Knoll 1999; Allwood et al. 2006; Van Kranendonk 2006, 2007). Modern stromatolites form by intermittent lithification of cyanobacterial mats (Reid et al. 2000), and there is clear evidence as far back as the Paleoarchean Era (>3.4 Ga) for microbially mediated carbonate mineralization in stromatolites. These distinctive fossil structures provide the most unambiguous case for localized Paleoarchean biomineralization.

Unambiguous Paleoarchean sedimentary carbonates occur as laminated stromatolitic dolomites in the 3.40 Ga Strelley Pool chert and as ankerite-chert beds in the 3.49 Ga Dresser Formation in the Pilbara Craton of Western Australia (Van Kranendonk et al. 2003; Allwood et al. 2006; Van Kranendonk 2007). However, in spite of ferroan carbonate formation, extensive sedimentary carbonates are uncommon in the geologic record until ~3.0 Ga, when the first dolostone [$CaMg(CO_3)_2$] units appear. One of the thickest Archean carbonate platforms occurs in the ~2.95 Ga Steep Rock Group of northwestern Ontario and preserves giant stromatolites (up to 5 to 10 m) with aragonite fans, calcite, and rare gypsum molds (Jolliffe 1955; Wilks and Nisbet 1988; Tomlinson et al. 2003). However, most limestone ($CaCO_3$) carbonate platforms do not appear until ~2.7 Ga (Sumner 1997), though it has been argued that earlier dolostones represent chemically replaced limestones (Tucker 1982; Grotzinger and Read 1983). Large dolomitic stromatolites occur in the 2.72 Ga Tumbiana Formation in Western Australia and specimens of these contain the oldest primary aragonite in the form of nanocrystals closely associated with organic globules (Lepot et al. 2008).

Metamorphism of platform limestones and dolostones produced marbles and new associated suites of Ca-Mg minerals. Of special note are the diverse carbonate skarn minerals produced by metasomatism and contact metamorphism with hot, near-surface igneous bodies. Distinctive carbonate skarn minerals include wollastonite ($CaSiO_3$), diopside ($CaMgSi_2O_6$), monticellite ($CaMgSiO_4$), grossular ($Ca_3Al_2Si_3O_{12}$), tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$], scapolite [$Ca_4Al_3Si_6O_{24}(CO_3,Cl,OH,SO_4)$], vesuvianite [$Ca_{10}(Mg,Fe,Mn)_2Al_4Si_9O_{34}(OH,Cl,F)_4$], and dozens of other species.

Sulfate mineralogy also played an important role in early Archean oceans. Sulfate is the ocean's second most abundant anion today, but its concentration has varied over time. Some sulfate was generated by atmospheric photolytic reactions in the anoxic atmosphere and delivered to the oceans (Farquhar et al. 2000), but the primary source was probably continental weathering, primarily from the early Paleoproterozoic Era onward (Habicht et al. 2002). Kah et al. (2004) estimate that sulfate levels in the Proterozoic ocean were only 5 to 15% of modern levels. In the absence of sulfate-reducing microbes, this sulfate would be primarily reduced to H_2S during hydrothermal circulation through mid-ocean ridges.

Barite ($BaSO_4$), a relatively insoluble mineral that precipitates from reaction of Ba leached from volcanic rocks and low levels of aqueous SO_4^{2-}, appears to be the only sulfate mineral that commonly survived from the Archean Eon. The oldest known barite deposits (3.5 to 3.4 Ga) are from South Africa, Western Australia, and India (Strauss 2003; Buick and Dunlop 1990; Van Kranendonk 2006). In addition to hydrothermal sulfates, evaporite sulfates such as anhydrite ($CaSO_4$) and gypsum [$CaSO_4 \cdot 2(H_2O)$] may have formed locally. Few ancient evaporite deposits have survived, although true Archean evaporites with the Na carbonate, nahcolite ($NaHCO_3$), were described from the Barberton Greenstone Belt (Tice and Lowe 2004) and from the Pilbara Craton in Western Australia (Sugitani et al. 2003). In addition, some researchers argue that North Pole (Western Australia) barite has replaced gypsum in a shallow marine evaporite setting (Buick and Dunlop 1990; Shen et al. 2001), although Van Kranendonk (2006) has presented evidence that the North Pole barite replaced sedimentary carbonate as a result of low-temperature (white smoker) hydrothermal alteration during exhalative cooling of the underlying felsic magma chamber.

The Paleoarchean sulfur cycle was undoubtedly influenced by biology, as well. Evidence from a large range of $\delta^{34}S$ values indicates microbial sulfur metabolism as early as 3.5 Ga in Western Australia (Shen et al. 2001; Phillippot et al. 2007). Smaller ranges of $\delta^{34}S$ values from the 3.8 Ga Isua formation do not unambiguously suggest microbial sulfur processing in the Eoarchean Era (Papineau and Mojzsis 2006). Huston and Logan (2004) have also suggested that biological processes played a role in barite deposition associated with some banded iron formations.

In spite of such possible influences of cellular life on the nature and distribution of carbonates, sulfates, and even granites, primitive microbes on the anoxic Archean Earth appear to have played a relatively minor role in modifying Earth's surface mineralogy. We estimate that by the end of the Neoarchean Era (2.5 Ga) Earth's near-surface environment hosted perhaps 1500 different mineral species, most of which could occur in near-surface environments of any volatile-rich anoxic terrestrial planet that had experienced cycles of granite formation and plate tectonics. However, this situation changed dramatically in the Paleoproterozoic Era with the advent of large-scale biologically mediated changes in ocean and atmospheric chemistry.

Minerals and the origin of life

The geochemical processes that led from a lifeless world to the chemical origin of life are not known. However, several scenarios for life's origins on Earth rely explicitly on minerals as templates, catalysts, and/or metabolites (e.g., Hazen 2005, 2006). Consequently, the origin of life on a terrestrial planet may require that the planet has first achieved some minimal degree of mineral evolution (Parnell 2004). The two mineral groups most often cited in this regard are clays (e.g., Lahav et al. 1978; Cairns-Smith and Hartman 1986; Ferris 1993; Hanczyc et al. 2003) and transition metal sulfides (Wächtershäuser 1992; Russell and Hall 1997; Cody et al. 2004). If common early stage minerals suffice for prebiotic processes, then they should be readily available early in the history of any wet terrestrial planet or moon. However, if specific exotic mineral species are required—i.e., mackinawite [$(Fe,Ni)S_{0.9}$] or griegite (Fe_3S_4) as cited by Russell and Hall (2002) and Cody (2004), or borates as proposed by Ricardo et al. (2004)—then a greater degree of mineral evolution may be required.

THE ERA OF BIOLOGICALLY MEDIATED MINERALOGY (2.5 GA TO PRESENT)

For most of the past 2.5 billion years, since the Paleoproterozoic Era, minerals at Earth's surface have co-evolved with life. Indeed, most of Earth's mineral diversity today may be a consequence, direct or indirect, of the biosphere.

Stage 7. The Paleoproterozoic "Great Oxidation Event" (2.5 to 1.9 Ga)

The rise of atmospheric oxygen in the Paleoproterozoic Era was one of the most significant irreversible events in Earth's history (Canfield et al. 2000; Kump et al. 2001; Kasting 2001; Kasting and Siefert 2002; Towe 2002; Holland 2002; Bekker et al. 2004; Barley et al. 2005; Catling and Claire 2005; Papineau et al. 2005, 2007; Kump and Barley 2007). A surge in tectonic activity likely occurred during the assembly of large continental landmasses (possibly a supercontinent) in the Neoarchean Era and during the onset of their break-up in the early Paleoproterozoic Era (Barley et al. 2005; Aspler and Chiarenzelli 1998). Elevated tectonic activity and rifting at that time may have perturbed the greenhouse-controlled climate by triggering a series of major glaciations. Higher tectonic activity combined with rapid climate change in the Paleoproterozoic Era would have accelerated erosion, which may have provided a critical source of nutrients in seawater to stimulate primary biological productivity at that time (Papineau et al. 2007).

This episode saw an increase in atmospheric oxygen in between major glaciations (Bekker et al. 2004; Papineau et al. 2007) and during a post-glacial period of carbon isotope excursion in carbonates until about 2.06 Ga (Karhu and Holland 1996). Atmospheric oxygenation in the Paleoproterozoic Era was principally a consequence of oxygenic photosynthesis by cyanobacteria, as the post-glacial period is characterized by an unprecedented increase in taxonomic diversity and expansion of stromatolites (Melezhik et al. 1997). Goldblatt et al. (2006) suggest that the early rise of cyanobacteria led to two simultaneously stable states for atmospheric oxygen and that this bistability arose from ozone shielding. According to their model, an increase in tropospheric ozone above a critical value resulted in effective ultraviolet shielding, causing a nonlinear increase in the half-life of atmospheric oxygen. This bistability might explain sulfur isotope evidence that points to a possible earlier transitory interval of minor oxygenation between 2.76 and 2.92 Ga (Ohmoto et al. 2006; Ono et al. 2007) and again at 2.51 Ga (Anbar et al. 2007; Kaufman et al. 2007). However, Farquhar et al. (2007) interpret changes in the mass independent fractionation of sulfur isotopes in the Mesoarchean Era (3.2 to 2.8 Ga) in terms of changes in atmospheric sulfur chemistry, not necessarily an episodic increase in oxygen.

Methanogenesis, both biotic and abiotic, may have also impeded Archean atmospheric oxidation. Serpentinization and microbial methanogenesis during the Archean Eon would have led to progressively higher atmospheric methane concentrations (Sherwood-Lollar et al. 1993, 2006; Catling et al. 2001; Kasting and Siefert 2002; Scott et al. 2004; Ueno et al. 2006)—perhaps as much as 600× present levels (Pavlov et al. 2003). The methane could have represented a significant greenhouse gas at the time, but should have fluctuated significantly during the glacial period in the early Paleoproterozoic Era (Claire et al. 2006; Papineau et al. 2005).

The Great Oxidation Event had irreversible consequences and a profound effect on Earth's near-surface mineralogy (Folinsbee 1982). In the aftermath of the Paleoproterozoic glaciations, carbonate deposits between 2.25 and 2.06 Ga contain some of the highest stromatolite diversity in Earth's history (Grotzinger and Knoll 1999; Melezhik et al. 1997), indicating robust microbial carbonate and phosphate biomineralization (Fig. 9). Carbonates in this time-period are also known to record a worldwide carbon isotope excursion, which is interpreted to indicate a significant accumulation of oxygen in the atmosphere (Karhu and Holland 1996).

Atmospheric oxygenation in the Paleoproterozoic Era led to large-scale deposition of oxidized hematitic BIFs as well as massive manganese deposits in marine environments. Between about 2.6 and 2.2 Ga, large BIF deposits formed in Western Australia, South Africa, and Brazil (Barley et al. 1997) simultaneously with the emplacement of numerous large igneous provinces and their dike swarms across Archean cratons (e.g., Heaman 1997; Bleeker and Ernst 2006). The world's largest economic sources of iron, which contain an estimated 90% of all Fe ore reserves, are BIFs ~2.5 to 1.85 Ga in age of the Lake Superior type (James and Trendall 1982). Notably this major event of BIF deposition occurred simultaneously with the emplacement of the giant Matechewan radiating dike swarms and correlative swarms on other cratons (Heaman 1997). Some BIF, carbonates, and other marine sediments deposited during and after the carbon isotope excursion in South Africa, Gabon, and India have high levels of manganese and constitute large economic deposits of minerals such as kutnahorite [$Ca(Mn,Mg,Fe)(CO_3)_2$], pyrolusite (MnO_2), rhodochrosite ($MnCO_3$), rhodonite [$(Mn,Fe,Ca)SiO_3$], bixbyite [$(Mn,Fe)_2O_3$], braunite ($Mn^{2+}Mn^{3+}_6SiO_{12}$), and hausmannite ($Mn^{2+}Mn^{3+}_2O_4$) (Leclerc and Weber 1980; Dasgupta et al. 1992; Tsikos and Moore 1997; Roy 2006). Iron minerals commonly encountered in Paleoproterozoic BIF include minnesotaite [$(Fe,Mg)_3Si_4O_{10}(OH)_2$], ferri-annite [$K(Fe,Mg)_3(Fe,Al)Si_3O_{10}(OH)_2$], riebeckite [$Na_2Fe_5Si_8O_{22}(OH)_2$],

FIGURE 9. The ~2.0 Ga Aravalli stromatolitic phosphorites of Udaipur, Rajasthan, India, likely reflect a period of elevated productivity due to high levels of nutrients associated with the Great Oxidation Event. Photo by D. Papineau.

chamosite [$(Fe,Mg)_5(Al_2Si_3O_{10}(OH,O)_8$], and ripidolite [$(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$]. The traditional interpretation of the cessation of BIF deposition at ~1.85 Ga is an increase in deep-ocean oxidation, which completely removed the source of upwelling Fe^{2+} (Cloud 1972; Holland 1984). However, deep ocean oxidation is not necessary to explain the end of BIF deposition, as it could have been due to an increased supply of H_2S from microbial sulfate reduction, which overcame the hydrothermal flux of iron to the deep ocean and resulted in sulfidic bottom waters (Canfield 1998; Poulton et al. 2004).

Enhanced oxidative weathering and increased redox states also had profound effects on the chemistry of coastal seawater. During the warm period in the aftermath of glaciations, oxidative weathering of sulfides exposed on the Archean crust led to the delivery of higher riverine sulfate fluxes to the ocean. Sulfur isotopes of sulfides in post-glacial sedimentary rocks suggest highly variable seawater sulfate levels (Bekker et al. 2004; Papineau et al. 2005, 2007) and sulfate minerals such as anhydrite and gypsum became more abundant in shallow marine environments (Cameron 1983; El Tabakh et al. 1999; Bekker et al. 2006). Weathering after the end of the Paleoproterozoic glacial epoch is also evidenced by widespread occurrences of Al-rich quartzite, which suggest a transition to greenhouse conditions (Bekker et al. 2006). Combined with high weathering rates and changing oceanographic patterns driven by climate change, increased redox conditions were also probably responsible for the formation of phosphatic sediments in shallow marine environments. Sedimentary phosphorites occur for the first time in the geological record after the rise of atmospheric oxygen (Bekker et al. 2003). The largest Paleoproterozoic phosphate deposits occur as ~2.0 Ga stromatolitic phosphorites embedded in dolomites in Rajasthan, India, and are composed mainly of carbonate fluorapatite (Banerjee 1971; Chauhan 1979). Other Paleoproterozoic phosphate-rich sedimentary deposits, which occur in the form of apatite-rich bands a few centimeters thick, are also associated with BIF in the Paleoproterozoic Era (Button 1982; Gehör 1994) and as small rounded masses of carbonate fluorapatite in ferruginous cherts that are possibly of microbial origin (Mancuso et al. 1975). Archean levels of oceanic phosphorus may have been lower than in the Paleoproterozoic Era, which could be a reflection of higher sequestration of phosphorus by adsorption onto iron oxides, such as in hydrothermal environments (Berner 1972; Wheat et al. 1996) and/or a smaller flux of riverine phosphorus (Bjerrum and Canfield 2002; cf. Konhauser et al. 2007b).

The Paleoproterozoic rise in atmospheric oxygen (and concomitant oxygenation of near-surface groundwater) likely represents the single most important event in the diversification of Earth's mineralogy. Of the ~4300 known mineral species, more than half are oxidized and hydrated weathering products of other minerals. A survey of the RRUFF database (http://rruff.info), which tabulates mineral species according to principal elements, underscores this point. Of 4259 approved mineral species tabulated (as of March 1, 2008), 2425 (57%) are hydrated products. For example, 256 of 321 known copper-oxide minerals are hydrated species, most of which likely resulted from weathering in an oxygen-rich environment. Thus, such distinctive copper minerals as chrysocolla [$(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot n(H_2O)$], turquoise [$CuAl_6(PO_4)_4(OH)_8 \cdot 4(H_2O)$], shattuckite [$Cu_5(SiO_3)_4(OH)_2$], chalcanthite [$CuSO_4 \cdot 5(H_2O)$], malachite [$Cu_2(CO_3)(OH)_2$], azurite [$Cu_3(CO_3)_2(OH)_2$], and brochanthite [$Cu_4(SO_4)(OH)_6$] may not have occurred to any significant extent prior to biological oxygenesis. Similarly, the database reveals that many minerals in metal ore bodies are associated with oxidative weathering. As many as 202 of 220 different uranium minerals, 319 of 451 minerals with Mn and O, 47 of 56 minerals with Ni and O, and 582 of 790 minerals with Fe and O are hydrated and oxidized. Many of these species are quite rare, some known from only a handful of specimens. Nevertheless, the biologically mediated Paleoproterozoic occurrence of many of these phases would have marked a significant rise in Earth's mineralogical diversity. In this view, it is possible that the majority of mineral species on Earth are biologically mediated through the effects of atmospheric oxidation, even though they are not biominerals directly produced by living cells.

Stage 8. The "intermediate ocean" (1.9 to 1.0 Ga)

The billion-year interval commencing ~1.9 Ga appears to have been a period of relative stasis in the mineral evolution of Earth. At ~1.85 Ga the production of banded iron formations ceased relatively abruptly, signaling a significant change in ocean chemistry likely driven by microbial activity. This gradual change to an "intermediate ocean"—an ocean of intermediate oxidation state—appears to have resulted from increased microbial sulfate reduction and surface oxidation (Anbar and Knoll 2002). On the one hand, relatively reducing surface conditions in the early Paleoproterozoic Era limited the solubility and weathering of continental sulfides, thus maintaining the relatively low H_2S concentration of the oceans. Increased atmospheric oxygen in the that era, on the other hand, might have led to delivery of sulfate to the deep ocean, where microbial sulfate reduction to H_2S led to the sulfidic (and hence anoxic) conditions.

Deep ocean anoxia would have been further maintained through the raining out of organic carbon, also the consequence of biological activity. The deep ocean thus would have become starved of Fe and other metals, not by oxidation, but through precipitation of insoluble metal sulfides. This latter scenario has important implications for life. Anbar and Knoll (2002) pointed out that such sulfidic deep-ocean conditions would have scavenged biologically important metals such as Fe and Mo (Scott et al. 2008), as well as phosphorus (Berner 1972; Wheat et al. 1996), thus restricting biological productivity in the Mesoproterozoic Era. Consequently, Proterozoic sulfide mineralization may have deterred the radiation of life for a billion years.

The late Paleoproterozoic to Mesoproterozoic Era (1.8 to 1.0 Ga) appears to have been a time of minimal mineralogical innovation. Many mineral forming processes had already evolved, and atmospheric and ocean chemistries appear not to have changed sufficiently to trigger significant new modes of mineralization. Even so, environmental and biological controls have been ascribed to the distribution of distinctive stratiform lead-zinc deposits in sedimentary environments of cratonic margins after about 1.8 Ga (Lyons et al. 2006), uranium deposits (with dozens of secondary minerals) derived from weathering of granitic rocks in Canada and Northern Australia at 1.8 to 1.1 Ga, and sedimentary copper deposits of the Zambian or "Kupferschiefer" (Central European) type at 1.4 to 0.2 Ga (Folinsbee 1982).

Stage 9. The Neoproterozoic snowball Earth and oxygenation events (1.0 to 0.542 Ga)

Multiple lines of evidence indicate that Earth experienced dramatic fluctuations in climate and atmospheric composition between about 1.0 and 0.542 Ga, with at least two (and possibly as many as four) "snowball Earth" events between about 0.75 and 0.54 Ga (Hoffman et al. 1998; Kennedy et al. 1998; Jacobsen 2001). Evidence includes extensive near-sea level, low-latitude glacial deposits (Young 1995; Hoffman and Prave 1996; Halverson 2005; Evans 2006), carbon and sulfur isotope excursions (Hoffman et al. 1998; Gorjan et al. 2000; Hurtgen et al. 2005; Fike et al. 2006), the occurrence of cap carbonate overlying glacial diamictites (Fairchild 1993; Kennedy 1996; Halverson et al. 2005), the distribution of iron minerals (Young 1976; Canfield et al. 2007), and Ir anomalies (Bodiselitsch et al. 2005). According to this so-called "snowball Earth" scenario (Kirschvink 1992; Hoffman and Schrag 2000), glacial cycles occurred during a period when continents, undergoing active rifting, were clustered near the equator. Partial snow cover triggered a runaway albedo feedback, possibly amplified by decreases in atmospheric CO_2 (Ridgwell et al. 2003; Donnadieu et al. 2004), that ultimately covered Earth in ice or slush. During global glaciations, life may have been more restricted, but phototrophic organisms and complex microbial communities ("biological refugia") persisted and were active in marine environments (Olcott et al. 2005).

Evidence from estimates of volcanic CO_2 fluxes at convergent margins (Caldeira 1991) and accumulated iridium in glacial deposits (Bodiselitsch et al. 2005) suggest that these snowball or slushball episodes lasted on the order of 10 million years. During those intervals, the hydrologic cycle must have slowed significantly. Meanwhile, as surface weathering processes slowed down, atmospheric concentrations of volcanic CO_2 increased to as high as 0.12 atmospheres (Caldeira and Kasting 1992; Pierrehumbert 2004). Ultimately, this CO_2 led to a rapid greenhouse warming, melting of the ice cover, and a dramatic episode of rapid cap carbonate deposition, including thick carbonate crystal fans of aragonite, which suggest highly supersaturated seawater (Fig. 10).

An increase in atmospheric oxygen, from <2% to ~15% of modern values, appears to have occurred immediately following glacial melting, based on high-resolution carbon and sulfur isotope data (Fike et al. 2006) and the sudden occurrence of deep-water iron oxide deposits (Canfield et al. 2007). Liang et al. (2006) proposed that this oxidation event resulted from the production of hydrogen peroxide by photochemical reactions involving water vapor, and its subsequent diffusion and sequestration in the ice until released during melting. An alternative hypothesis is that an increased weathering flux of phosphorus to the oceans after glaciations stimulated photosynthetic oxygen production (Lenton and Watson 2004). This model may be supported by biomarker evidence for algal blooms in the aftermath of snowball glaciation, where post-glacial weathering could have delivered massive amounts of nutrients to seawater (Elie et al. 2007). The inferred increase in the relative rate of organic

FIGURE 10. Neoproterozoic snowball Earth glaciation events are documented in sequences of glacial deposits (lower slopes) overlain by cap carbonates (cliff faces) with aragonite crystal fans. This sequence is from the Skeleton Coast of Namibia. Photo courtesy of P. Hoffman (www.snowballearth.org).

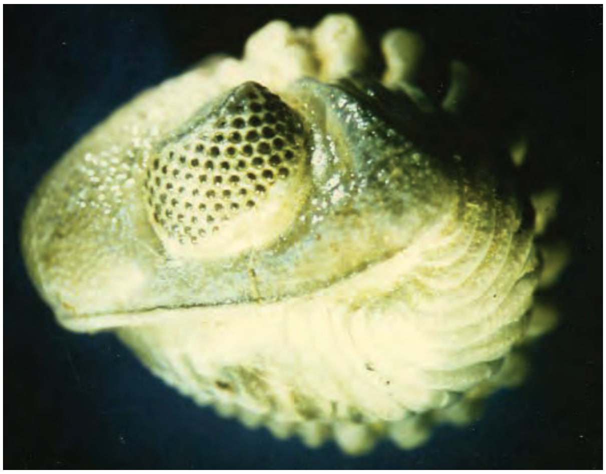

FIGURE 11. The compound eyes of the phacopid trilobite Eldgredops rana from the Silurian Silica Shale of Silica, Ohio, are formed from rows of calcite single crystals with the *c* axes aligned parallel to the lens axis. Individual lenses have been found to display variable Mg content that is zoned in such a way as to reduce chromatic aberration. Photo by R. Hazen.

carbon burial in Neoproterozoic carbonates (e.g., Halverson et al. 2005; DesMarais et al. 1992) may also be consistent with the latter scenario. In any case, the Neoproterozoic increase of atmospheric oxygen was essential to the rise of large oxygen-breathing animals (e.g., Runnegar 1991; Canfield et al. 2007).

Whatever the source, the Neoproterozoic cyclic episodes of cooling and global glaciation, atmospheric CO_2 enrichment, greenhouse warming, and oxygenation had significant effects on surface mineralogy. Among the most intriguing mineralogical proposals related to Neoproterozoic oxygenation is the so-called "clay mineral factory" (Kennedy et al. 2006). It is well established that microbial activity enhances clay mineral production, for example by the bio-weathering of feldspar and mica (Schwartzman and Volk 1989; Bennett et al. 1996; Paris et al. 1996; Barker et al. 1998; Ueshima and Tazaki 1998; Ueshima et al. 2000; Tazaki 2005). Kennedy et al. (2006) observe a significant increase in clay mineral deposition in the Neoproterozoic that may have been the result of increased microbial activity in soils. An important consequence of this clay mineral production is the enhanced marine sequestration of organic carbon adsorbed onto clay surfaces (Hedges and Keil 1995; Mayer et al. 2004). Oxidation of organic carbon represents an important sink for atmospheric oxygen; hence clay-mediated burial of organic carbon may have contributed to the rise in atmospheric oxygen. Note also that in the context of mineral evolution, weathering in soils produces a suite of clay minerals—i.e., smectite [$(Na,Ca)_{0.3}(Al,Mg)_{4-6}(Si,Al)_8O_{20}(OH)_4$] and kaolinite [$Al_2Si_2O_5(OH)_4$]—quite distinct from that of the serpentine-chlorite mineralogy characteristic of hydrothermal alteration (Weaver 1989; Chamley 1989). Thus, the postulated clay mineral factory represents an irreversible change in both the total clay production and the relative abundances of different clay minerals.

Enhanced oxidative weathering of sulfides during the Neoproterozoic period of cyclic glaciations is likely responsible for the increased abundance of seawater sulfate at that time (Canfield and Teske 1996; Hurtgen et al. 2005; Fike et al. 2006; Halverson and Hurtgen 2007). Concomitantly, the supply of phosphorus by rivers to the oceans should have created new opportunities for photosynthetic organisms and biomineralization. Large sedimentary phosphorite deposits are restricted to time intervals when oceanic circulation experienced dramatic changes, such as in the late Neoproterozoic-early Cambrian. Stagnation of the oceans during snowball Earth events was followed by periods of vigorous circulation, which could have been conducive to phosphorite production (Donnelly et al. 1990). Major Neoproterozoic/early Cambrian phosphorite deposits occur in North and South America, Africa, Europe, Asia, and Australia (Notholt and Sheldon 1986), and also stratigraphically overlie glacially derived sedimentary rocks (Cook and Shergold 1984). For instance, phosphorites occur stratigraphically near and above tillites in the Australian Adelaide Geosyncline (Howard 1986), in the Chinese Doushantuo Formation (Yueyan 1986), in the West African Volta and Taoudeni Basins (Flicoteaux and Trompette 1998), and in the Brazilian São Francisco Supergroup (Dardenne et al. 1986; Misi et al. 2006). These occurrences suggest yet another connection between climate change and the abundance of phosphorus in seawater that can lead to mineralogical changes.

Stage 10. Phanerozoic biomineralization (<0.542 Ga)

By the beginning of the Phanerozoic Eon (0.542 Ga) biology came to dominate the mineralogical diversification of Earth's surface. A comprehensive review of Phanerozoic biominerals, which are "the products of selective uptake of elements from the local environment and their incorporation into functional structures under strict biological control" (Mann 2001; Perry et al. 2007), is beyond the scope of this review (but see Dove et al. 2003). Examples of the formation of more than 60 minerals mediated by microbes, plants, invertebrates, and vertebrates [including more than two dozen in humans (Yoder 2002)] will serve to illustrate the richness of the subject (Table 3).

Of greatest significance in terms of rock volume, the early Cambrian saw the abrupt rise of all major skeletal minerals (calcite, aragonite, magnesian calcite, apatite, and opal), and few new types have appeared since then (Runnegar 1987; Knoll 2003b). Volumetrically, calcium carbonates represent the most significant biominerals. Of special note in this regard was the evolution of planktonic calcifiers, which for the first time provided a steady source of $CaCO_3$ to deep ocean sediments, thus reducing the episodic formation of shallow-water sedimentary (cap) carbonates. This buffering of ocean carbonate-ion concentration moderated glacial events and reduced the likelihood of future snowball events (Ridgwell et al. 2003). In the Phanerozoic Eon, for the first time in Earth's history carbonate deposition in the deep oceans was comparable to that in shallow ocean environments.

A significant mineralogical novelty related to biologically mediated carbonates is the variable biomineralization of calcium carbonate by corals, mollusks, and other invertebrates (Knoll 2003b). Calcite is observed to dominate from the Cambrian through early Carboniferous, but a dramatic and sudden shift to aragonite biomineralization is observed in the late Paleozoic through the mid-Jurassic. Calcite again became the dominant biocarbonate after the mid-Jurassic (Stanley and Hardie 1998). For example, both rugose corals, which thrived prior to their eventual extinction at the terminal Permian event, and Mesozoic scleractinian corals have calcitic skeletons. Modern scleractinian corals, by contrast, are composed of aragonitic skeletons (Stolarski et al. 2007). Modern mollusks, which display similar variation in their skeletal mineralogy, use macromolecules (glycoproteins) to control the precipitation of aragonite vs. calcite (Falini et al. 1996; Cohen and McConnaughey 2003). These shifts have been attributed to variations in ocean chemistry, when the Mg/Ca mole ratio is >2 aragonite and Mg-calcite are favored (Stanley and Hardie 1998).

Magnesium-bearing carbonates are also incorporated into bioskeletons. For example, some sulfate-reducing microbes precipitate dolomite directly from anoxic solutions (Warthmann et al. 2000). Remarkably, the compound eyes of some phacopid trilobites (Fig. 11), which are formed from rows of calcite single crystals with the *c* axes aligned parallel to the lens axes, display variable Mg content that is zoned in such a way as to reduce chromatic aberration (Clarkson and Levi-Setti 1975; Lee et al. 2007).

A variety of phosphate minerals (Table 3), notably hydroxylapatite [$Ca_5(PO_4)_3(OH)$] and whitlockite [$Ca_{18}H_2(Mg,Fe)_2(PO_4)_{14}$], serve as skeletal minerals in both vertebrates (i.e., as the principal minerals in teeth and bones) and invertebrates (for example, in the shells of inarticulate brachiopods; Knoll 2003b). Microbial precipitation of phosphates, predominantly hydroxylapatite but also carbonate fluorapatite (Schulz and Schulz 2005), played the dominant role in the formation of what are now commercial phosphorite deposits (Zhao et al. 1985; Burnett and Riggs 1990; Cook and Shergold 1990).

The history of clay mineralization provides another important example of the increasing importance of biological activity through time. Phanerozoic production of clay minerals in soils, especially since the advent of land plants in the Siluro-Devonian Period, is estimated to have been at least an order of magnitude greater than that of previous eras (Schwartzman and Volk 1991; Bennett et al. 1996; Paris et al. 1996; Barker et al. 1998; Tazaki 2005). This increase, which is an extension of the "clay mineral factory" hypothesis and associated rise of oxygen (Kennedy et al. 2006), is a distinctive aspect of post-Ordovician mineralogy. Indeed, evidence suggests that atmospheric oxygen concentrations have continued to rise during the Phanerozoic Era, especially in the Permo-Carboniferous (Berner et al. 2000). Falkowski et al. (2005) exploited carbon isotope data to estimate that atmospheric oxygen increased from ~10 to more than 20 mol% over the past 205 Ma.

Phanerozoic mineralogical novelty is enhanced by more than a dozen organic minerals, which have been identified from coal, black shales, oil shales, and other carbon-rich fossil sources. These biologically derived minerals include the remarkable Ni-porphyrin abelsonite ($Ni^{2+}C_{31}H_{32}N_4$), the purine uricite ($C_5H_4N_4O_3$), and several hydrocarbons ranging in size from kratochvilite ($C_{13}H_{10}$) to carpathite ($C_{24}H_{12}$). Perry et al. (2007) have also introduced the term "organomineral" to designate a "mineral product containing organic carbon," but "not directly produced by living cells." As examples they cite carbon-bearing siliceous hot-spring deposits, desert varnish, stromatolites, and a variety of trace fossils.

In addition to oxygenation, microbes in the Phanerozoic Era are likely to have played many roles in modifying Earth's near-surface mineralogy, and today the geochemical cycles of most elements are affected by biology (Banfield and Nealson 1997; Banfield et al. 1998; Frankel and Bazylinski 2003). Among the many ways that biology influences mineralogy, airborne microbes may play a dominant role in the nucleation and growth of ice particles in clouds and in subsequent snowfall (Christner et al. 2008). Microbial colonies can also form biofilms and colloids with large negatively charged reactive surface areas that may adsorb metals and precipitate various minerals. Microbes that catalytically oxidize pyrite and produce acidic waters may increase dissolution and precipitation reaction rates by six orders of magnitude (Singer and Stumm 1970; Nordstrom and Southam 1997). Even gold geochemistry may be strongly affected by biological activity; Reith et al. (2006) find that microbes can both solubilize gold (see also Lyalikova and Mockeicheva 1969; Korobushkina et al. 1983) and trigger the precipitation of secondary gold grains from aqueous $AuCl_4^-$ in shallow crustal environments. Thus, gold deposits may be enriched by microbial activity, and it is possible that some gold nuggets are the ultimate weathered consequence of subsurface biological processing.

TABLE 3. Names and idealized chemical compositions of selected minerals produced by biological mineralization processes (expanded from Dove and Weiner 2003, Table 1)

Name	Formula
Elements	
α-sulfur	S
γ-sulfur (Rosickyite)	S
Carbonates	
Amorphous calcium carbonates (at least 5 forms)	$CaCO_3{\cdot}H_2O$ or $CaCO_3$
*Aragonite	$CaCO_3$
*Calcite	$CaCO_3$
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$
Lansfordite	$MgCO_3{\cdot}5H_2O$
Magnesite	$MgCO_3$
Mg-calcite	$(Mg_xCa_{1-x})CO_3$
*Monohydrocalcite	$CaCO_3{\cdot}H_2O$
Nesquehonite	$Mg(CO_3){\cdot}3H_2O$
Protodolomite	$CaMg(CO_3)_2$
Rhodochrosite	$MnCO_3$
Siderite	$FeCO_3$
*Vaterite	$CaCO_3$
Phosphates	
Amorphous calcium phosphate	variable (at least 6 forms)
Amorphous calcium pyrophosphate	$Ca_2P_2O_7{\cdot}2H_2O$
Bakhchisaraitsevite	$Na_2Mg_5(PO_4)_4{\cdot}7H_2O$
*Brushite	$Ca[PO_3(OH)]{\cdot}2H_2O$
*Carbonate-hydroxylapatite	$Ca_5(PO_4,CO_3)_3(OH)$
Chlorapatite	$Ca_5(PO_4)_3Cl$
*Fluorapatite	$Ca_5(PO_4)_3F$
*Hannayite	$Mg_3(NH_4)_2H_4(PO_4)_4{\cdot}8H_2O$
*Hydroxylapatite	$Ca_5(PO_4)_3(OH)$
*Monetite	$Ca[PO_3(OH)]$
*Newberryite	$Mg[PO_3(OH)]{\cdot}3H_2O$
Octacalcium phosphate	$Ca_8H_2(PO_4)_6$
*Struvite	$Mg(NH_4)(PO_4){\cdot}6H_2O$
Hazenite	$KNaMg_2(PO_4)_2{\cdot}14H_2O$
Vivianite	$Fe_3^{2+}(PO_4)_2{\cdot}8H_2O$
*Whitlockite	$Ca_{18}H_2(Mg,Fe)_2(PO_4)_{14}$
Sulfates	
Aphthitalite	$K_3Na(SO_4)_2$
Ardealite	$Ca_2[PO_3(OH)](SO_4){\cdot}4H_2O$
Barite	$BaSO_4$
Celestine	$SrSO_4$
*Epsomite	$MgSO_4{\cdot}7H_2O$
*Gypsum	$CaSO_4{\cdot}2H_2O$
*Hexahydrite	$MgSO_4{\cdot}6H_2O$
Jarosite	$KFe_3^{3+}(SO_4)_2(OH)_6$
Melanterite	$Fe^{2+}SO_4{\cdot}7H_2O$
Schwertmannite	$Fe^{3+}_{16}O_{16}(OH)_{9.6}(SO_4)_{3.2}{\cdot}10H_2O$
Nitrates	
Gwihabaite	$(NH_4)NO_3$
Sulfides	
Acanthite	Ag_2S
Amorphous pyrrhotite	$Fe_{1-x}S$ ($x = 0 - 0.17$)
Galena	PbS
Greigite	Fe_3S_4
Hydrotroilite	$FeS{\cdot}nH_2O$
Mackinawite	$(Fe,Ni)_9S_8$
Marcasite	FeS_2
Pyrite	FeS_2
Pyrrhotite	Fe_7S_8
Orpiment	As_2S_3
Sphalerite	ZnS
Wurtzite	ZnS

* Minerals found in humans (after Yoder 2002).

In addition to numerous examples of indirect biologically mediated mineral formation, more than 60 minerals are known to be formed directly by intra-, inter-, and extracellular processes (Table 3), including several mineralogical rarities. For example, Akai et al. (1999) describe direct microbial precipitation of alternating (possibly seasonal) layers of the distinctive iron

TABLE 3.—*CONTINUED*

Name	Formula
Oxides	
Amorphous iron titanate	$Fe^{2+}TiO_3$
Amorphous iron oxide	Fe_2O_3
Amorphous manganese oxide	Mn_3O_4
*Anatase	TiO_2
Ilmenite	$FeTiO_3$
*Maghemite	$Fe_{2.67}O_4$
*Magnetite	Fe_3O_4
*Periclase	MgO
Ice	H_2O
Hydroxides and hydrous oxides	
Birnessite	$NaMn_4O_8{\cdot}3H_2O$
*Brucite	$Mg(OH)_2$
Ferrihydrite	$Fe_{4–5}(OH,O)_{12}$
Goethite	α-$FeO(OH)$
Lepidocrocite	γ-$FeO(OH)$
Todorokite	$NaMn_6O_{12}{\cdot}3–4H_2O$
Chlorides	
Atacamite	$Cu_2Cl(OH)_3$
*Halite	$NaCl$
*Sylvite	KCl
Fluorides	
Fluorite	CaF_2
Hieratite	K_2SiF_6
Silicates	
Amorphous silica	$SiO_2{\cdot}nH_2O$
*Quartz	SiO_2
Organic crystals*	
Abelsonite	$Ni^{2+}C_{31}H_{32}N_4$
Ca malate	$C_4H_4CaO_5$
Ca tartrate	$C_4H_4CaO_6$
Carpathite	$C_{24}H_{12}$
Earlandite	$Ca_3(C_6H_5O_7)_2{\cdot}4H_2O$
Glushinskite	$MgC_2O_4{\cdot}2H_2O$
Guanine	$C_5H_3(NH_2)N_4O$
Hartite	$C_{20}H_{34}$
Hoganite	$Cu(CH_3COO)_2{\cdot}H_2O$
Idrialite	$C_{22}H_{14}$
Kratochvílite	$C_{13}H_{10}$
Lindbergite	$MnC_2O_4{\cdot}2H_2O$
Moolooite	$CuC_2O_4{\cdot}nH_2O$
Paceite	$CaCu(CH_3COO)_2{\cdot}6H_2O$
Paraffin hydrocarbon	
Sodium urate	$C_5H_3N_4NaO_3$
*Urea	$CO(NH_2)_2$
Uricite	$C_5H_4N_4O_3$
*Weddelite	$CaC_2O_4{\cdot}2H_2O$
*Whewellite	$CaC_2O_4{\cdot}H_2O$

* Minerals found in humans (after Yoder 2002).

sulfate jarosite [$KFe_3^{3+}(SO_4)_2(OH)_6$] and goethite [$FeO(OH)$] at the Gunma iron mine in Japan. Jaws of the marine bloodworm Glycera dibranchiata contain the rare copper mineral atacamite [$Cu_2(OH)_3Cl$] (Lichtenegger et al. 2002). Microbes and multicellular organisms produce intercellular magnetic grains of the unusual sulfide greigite (Fe_3S_4), as well as magnetite (Chang and Kirschvink 1989; Pósfai et al. 1998; Thomas-Keprta et al. 2001; Lins et al. 2007; Coker et al. 2008). And several minerals, including various organic minerals, γ-sulfur, and hazenite [$KNaMg_2(PO_4)_2{\cdot}14H_2O$] (Table 3), may occur exclusively as microbially generated minerals.

DISCUSSION

Mineral evolution occurs on all solar system objects, but in particular on terrestrial planets and moons, in a variety of guises. The most obvious change over time, which is emphasized in this paper, is the increasing number of different mineral species. However, Earth's mineralogy has also changed in other respects, including the relative abundances of near-surface minerals, the diversity of mineral associations, the compositional ranges of minerals displaying solid solution, and the grain sizes and morphologies of minerals. For example, SiO_2 initially appeared as rare micro-grains of cristobalite in chondrites, then as dispersed millimeter-sized grains of quartz in some achondrites, and eventually as common centimeter-sized crystals in granitoids and megacrysts in pegmatites. Various forms of SiO_2 also accumulated in sediments, were transformed to stishovite and coesite in impacts, were metamorphosed in quartzites, and became important in bioskeletons. Feldspar minerals display similar increases in associations and grain sizes, while expanding greatly in compositional extent from Ca-rich feldspars in chondrites, to the full range of Ca-Na plagioclase in achondrites, to Na-K alkali feldspars in the subsequent evolution of igneous rocks on Earth. Thus the concept of mineral evolution incorporates more than just the diversity of mineral species.

Three processes that drive mineral evolution

The evolution of Earth's near-surface mineralogy results primarily from three principal processes. First are separation and concentration processes, for example planetary differentiation, outgassing, fractional crystallization, partial melting, crystal settling, and leaching by aqueous fluids. These processes led to diversification of the initially homogeneous element distribution in the pre-solar nebula into a broad spectrum of bulk compositions. As previously dispersed elements became selected and concentrated, new suites of minerals invariably emerged. Note that separation and concentration of an element only creates a new mineral when the volume of new composition exceeds some minimum spatial dimension. In this regard, it is likely that the stages and timing of mineral evolution would be somewhat different if one considers nano-scale minerals. Continuing studies of the distribution of minor and trace elements in undifferentiated meteorites will provide important insights on this size aspect of mineral evolution.

The second process that drives mineral evolution on terrestrial planets and moons is the emergence of an increased range of intensive variables, including temperature, pressure, and the activities of volatiles such as H_2O, CO_2, and O_2. On Earth, the range of these variables is reflected in the formation of such varied environmental regimes as ice caps, dry lakes, high-pressure metamorphic terrains corresponding to exhumed subduction zones, deep-ocean hydrothermal ecosystems, impact sites, and continental climate zones.

Finally, processes in living organisms have created and sustained both local and global compositional gradients that promote reaction pathways leading to new minerals. Note that both prebiotic and biologically mediated mineral diversification represents minimization of Gibbs free energy under new combinations of temperature, pressure and composition. In biological systems, however, new minerals may be catalyzed by living organisms in highly localized volumes that are not in equilibrium with the surrounding geochemical milieu (e.g., the biological precipitation of aragonite in shallow marine environments).

Comparative planetology

The general principles observed for the emergence of mineralogical complexity on Earth apply equally to any differentiated asteroid, moon, or terrestrial planet. In every instance mineral evolution will occur in a logical progression as a result of local, regional, and global processes (i.e., the stages outlined in Table 1 and Fig. 1). The degree to which a body will advance in mineralogical complexity beyond the relatively simple achondrite stage is dictated by the nature and intensity of subsequent cycling (and hence repeated separation and concentration of elements). Consequently, a planet's surface mineralogy will directly reflect the extent to which cyclic processes, including igneous differentiation, granitoid formation, plate tectonics, atmospheric and oceanic reworking (including weathering), and biological influences, have affected the body's history.

Arguably the single most important cause for mineralogical diversification is Earth's surface oxygenation associated with biological activity, which may be responsible directly or indirectly for more than two thirds of all known mineral species. Thus, for at least the last 2.5 billion years, and possibly since the emergence of life, Earth's mineralogy has evolved in parallel with biology. Accordingly, remote observations of the mineralogy of other moons and planets may provide crucial evidence for biological influences beyond Earth.

A comment on the term "evolution"

The use of the term "evolution" in the context of mineralogy may strike some readers as odd, perhaps even inappropriate. In spite of similar previous geological applications [notably Norman Bowen's (1928) *The Evolution of the Igneous Rocks*], the word continues to have contentious overtones (e.g., Ayala et al. 2008). Part of the difficulty is semantic, for "evolution" has at least half a dozen different social and technical meanings (Scott 2004, Chapter 2). At the most basic level, evolution is simply defined as "change over time," and in this respect there can be no question that mineral evolution has occurred. However, we suggest that mineral evolution implies something more, as it arises in part from a sequence of deterministic, irreversible processes that lead from the mineralogical parsimony of the pre-solar era to progressively more diverse and complex phase assemblages. In this sense, mineral evolution is a fascinating specific example of the more general process of cosmic evolution (Chaisson 2001; Morowitz 2002; Zaikowski and Friedrich 2008).

Nevertheless, mineral evolution is not analogous to biological evolution through Darwinian natural selection (Darwin 1859). In spite of creative suggestions to the contrary (e.g., Cairns-Smith 1982; Cairns-Smith and Hartman 1986), minerals do not mutate or compete for geochemical niches in the biological sense, nor do they pass information to progeny through a genetic mechanism. For example, quartz does not out-compete olivine for crystallization from granite magma. Minimization of Gibbs free energy simply leads to nucleation and growth of quartz, but not olivine. The driving force for mineral evolution, rather, is the evolving diversity of prebiotic and biologically mediated temperature-pressure-composition environments.

Complex evolving systems

Systems that evolve from relatively simple states to those of increasing complexity are a recurrent characteristic of the physical world (Zaikowski and Friedrich 2008). Examples include the evolution of chemical elements through stellar nucleosynthesis (Olive 2008); prebiotic organic chemical evolution (Hazen 2005); the evolution of technologies through invention, technology transfer, and competitive selection (Eldredge 2002); the evolution of languages (Dixon 1997; Atkinson et al. 2008); and the evolution of life (Futuyma 2005). The diversification of the mineral realm over 4.5 billion years of Earth history displays intriguing similarities, as well as important differences, to these and other complex evolving systems. In this context, mineral evolution has the potential to inform efforts to identify and quantify principles that underlie all complex evolving systems.

A detailed analysis of the properties of evolving systems is beyond the scope of this introductory review, but three essential aspects of many evolving systems—selection, punctuation, and extinction—are worth noting in the context of mineral evolution.

Selection. Complex systems commonly arise through the interaction of numerous individual components, or "agents" with their environment (Morowitz 2002; Hazen 2005, 2008). In such systems, agents are intrinsically able to adopt combinatorially large numbers of different states, yet only a relatively small fraction of these configurations are observed as a consequence of selection rules (e.g., Morowitz 2002; Hazen et al. 2007). Thus, neutrons and protons assemble into only a few hundred stable isotopic species, while the 83 geochemically stable chemical elements combine to form only a few thousand mineral species. Stochastic processes may influence the specific outcomes of some selective events, but selection is guided by physical and chemical principles and thus, by definition, is not random.

Punctuation. The proposal by Eldredge and Gould (1972) that biological evolution may at times occur in rapid spurts of innovation, or "punctuated equilibrium," is now recognized as a common theme in a variety of complex systems, including nucleosynthesis (Olive 2008), technological innovations (Eldredge 2002), and language (Dixon 1997; Atkinson et al. 2008). A similar phenomenon is observed in mineral evolution. Key irreversible events in Earth's history—planetary differentiation at 4.5 Ga and subsequent formation of the atmosphere and hydrosphere, the initiation of subduction at >3.0 Ga, major atmospheric oxidation events at around 2.2 and 0.6 Ga, and the emergence of a terrestrial biota in the Phanerzoic Era, for example—forever altered Earth's mineralogical landscape. Each event changed the distribution and initiated a jump in the diversity of Earth's near-surface mineralogy. Thus, as in other evolutionary systems, mineral diversity vs. time may have the punctuated character of a step function rather than a continuous increase.

Extinction. Extinction, the selective disappearance of some states, is a recurrent feature of many evolving systems. New technological innovations inevitably replace the old, some words become obsolete, and biological species eventually die out. Is the same true of mineral phases? Mineral evolution points to the fact that many mineral species had a specific time of first appearance on Earth, but is it likely that some near-surface species become unstable and disappear permanently from a terrestrial planet?

Some mineral-forming processes, for example those that formed the unusual reduced minerals of enstatite chondrites (Table 2), have ceased. These phases, which are unstable at Earth's oxidized surface, are now found only because of the continuing flux of EH chondrites. Nevertheless, given that surface temperatures throughout Earth's history have spanned the range from water ice to water vapor, and that most, if not all, of Earth's mineral forming processes (i.e., continued delivery of varied meteorites to the surface, igneous and metamorphic processes, plate tectonics, surface weathering, and microbial metabolism, for example) are still in play, Earth's mineralogical diversity has likely not diminished significantly. Indeed, one would be hard pressed to postulate a single mineral species that once was found in a near-surface environment but no longer exists.

Nevertheless, the permanent disappearance of species must have played a significant role in the mineral evolution of some terrestrial planets. Venus, for example, may have had a water-rich and clement surface environment early in its history (Ingersoll 1969; Donahue and Pollack 1983; Grinspoon 1997). However, the gradual loss of water (via hydrogen escape) and subsequent runaway CO_2-mediated greenhouse effect with present day surface temperatures of 480 °C must have resulted in the loss of some low-temperature and hydrous mineral phases (Johnson and Fegley 2000, 2003). For example, hydrated magnesium sulfates ($MgSO_4{\cdot}nH_2O$), including kieserite, starkeyite, hexahydrite, epsomite, and meridianiite (with $n = 1$, 4, 6, 7, and 11, respectively) are observed in carbonaceous chondrites, hypersaline environments on Earth, and possibly on the surface of Mars (Kargel 1991; Fortes 2005; Peterson et al. 2007). They were likely also once present on the surface of Venus, but in the present dry, high-temperature environment they (and hundreds of other hydrous minerals) are no longer stable phases.

Given these and other parallels between mineral evolution and the behavior of other living and non-living complex systems, the search for unifying evolutionary principles will provide a continuing motivation for studying the history of Earth's changing mineralogical landscape.

CONCLUDING REMARKS: FRAMING MINERAL SCIENCES

For more than a century, mineralogists have framed their science primarily in terms of equilibrium chemical and physical properties. Dana's systematic chemical classification and related schemes (Hurlbut 1971; Deer et al. 1996; Gaines et al. 1997) rely on the principal anion (silicates, carbonates, halides, etc.) to divide the mineral kingdom into chemically related groups of species. Further classification based on crystal chemical criteria (i.e., orthosilicates, cyclosilicates, biopyriboles, etc. for silicates) serves to subdivide groups of minerals according predominant topological motifs (Liebau 1985; Putnis 1992; Nesse 2000). Equilibrium phase diagrams amplify this approach by defining conditions of stability under which individual minerals form and groups of minerals coexist. This versatile approach to framing the subject of mineralogy, by combining equilibrium crystal chemical and thermodynamic considerations, underscores the close relationships between a mineral's physical properties and the arrangement of its atoms. Nevertheless, by adopting this sometimes static framing of our science, an inherent drama and excitement of mineralogy may be lacking.

Mineral evolution represents an alternative approach to systematizing—and to teaching—the subject of mineralogy. The mineral diversity of terrestrial planets evolves as a consequence of the dynamic histories of planets. Epic physical, chemical, and biological processes—planetary accretion and differentiation, plate tectonics and associated large-scale reworking of the lithosphere, and the origin and evolution of life—create gradients in temperature, pressure, and composition that selectively process elements and lead to new equilibrium mineral species. In this approach, the chronological stage of planetary evolution and the associated paragenetic processes that lead to distinctive suites of minerals, rather than the equilibrium structure, composition, and properties of the minerals themselves, is the underlying organizing principle. Geologic time becomes a central parameter of mineralogy.

This is not to say that core chemical and physical processes are not vital to mineralogy. Consider the dozen or so earliest mineral phases to appear in the pre-solar nebulae (Table 2a). These "ur-minerals"—the logical starting point of any mineral evolution course—manifest a variety of bond types (metallic bonds, covalent bonds, ionic bonds, and van der Waals interactions), while they also incorporate structural motifs (e.g., coordination polyhedra of Si, Mg, Al, and Ca) that are common to many rock-forming phases. These dozen species also illustrate such key mineralogical concepts as solid solution, order-disorder, and polymorphism. These characteristics, coupled with the relatively simple phase relationships that lead to their condensation, provide a rich context by which to introduce the chemical and physical principles that are fundamental to all mineralogy. However, unlike traditional mineralogy curricula, these principles are introduced as part of a larger evolutionary story.

Consider as an example the silicate garnet group of minerals, $X^{2+}_3Y^{3+}_2Si_3O_{12}$, which share the same structure and are thus traditionally lumped together in mineralogy texts. From the perspective of mineral evolution, however, different garnet-structured phases are scattered across several different mineralogical stages. Majorite and its Mg-isomorph [$Mg_3(FeSi)Si_3O_{12}$ and $Mg_3(MgSi)Si_3O_{12}$, respectively], which form by the impact metamorphism of pyroxene in meteorites and asteroids, must have appeared in the earliest stages of mineral evolution. Grossular ($Ca_3Al_2Si_3O_{12}$) arose shortly thereafter during thermal alteration of chondrites, as did andradite ($Ca_3Fe_2Si_3O_{12}$) in achondrites. Pyrope ($Mg_3Al_2Si_3O_{12}$), a principal mineral phase in deep-formed ecologite, may have appeared on Earth's surface as a result of volcanic transport as early as stage 3, while almandine ($Fe_3Al_2Si_3O_{12}$), the common red garnet of peraluminous granites, is representative of stage 4. Spessartine ($Mn_3Al_2Si_3O_{12}$) is associated with uplifted and eroded regional metamorphic terrains, and thus may have required the lateral tectonics of stage 5. We conclude that garnet group minerals are not all closely related in their mineral evolution context; their crystal chemistries are similar, but their stories are vastly different. Thus the garnet structure represents the motif of a mineralogical rondo that returns again and again in different geological settings throughout Earth's history, up to and including the modern synthesis of yttrium aluminum garnet (YAG) and other technological garnets. Similar arguments could be made for the diverse evolutionary histories of individual members of olivines, pyroxenes, feldspars, clay minerals, sulfides, carbonates, and most other groups of rock-forming minerals.

Mineral evolution complements more traditional approaches to teaching mineralogy by providing an historical narrative for each mineral phase. The 4.5 billion year story integrates the principal themes of planetary science: geodynamics, petrology, geochemistry, thermodynamics, and geobiology. As such, mineralogy becomes key to unlocking our planet's history, and thus assumes its rightful central role in the Earth sciences.

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