

Clay mineral evolution

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ABSTRACT

Changes in the mechanisms of formation and global distribution of phyllosilicate clay minerals through 4.567 Ga of planetary evolution in our solar system reflect evolving tectonic, geochemical, and biological processes. Clay minerals were absent prior to planetesimal formation ~4.6 billion years ago but today are abundant in all near-surface Earth environments. New clay mineral species and modes of clay mineral paragenesis occurred as a consequence of major events in Earth's evolution—notably the formation of a mafic crust and oceans, the emergence of granite-rooted continents, the initiation of plate tectonics and subduction, the Great Oxidation Event, and the rise of the terrestrial biosphere. The changing character of clay minerals through time is thus an important part of Earth's mineralogical history and exemplifies the principles of mineral evolution.

Keywords: Clay minerals, biominerals, weathering, diagenesis, Mars mineralogy

INTRODUCTION

The mineralogy of terrestrial planets, moons, and asteroids diversified as physical, chemical, and (in the case of Earth) biological processes modified the initially relatively homogeneous material of the solar nebula into differentiated zones of varied temperature, pressure, and composition. Earth's 4.567 billion year history, as a consequence, can be divided into three eras and 10 stages of mineral evolution, each of which has seen significant changes in the planet's near-surface mineralogy (Hazen et al. 2008, 2011; Table 1). These dramatic changes include diversification in the number of different mineral species; shifts in the distribution of those species; systematic changes in major, minor, and trace element compositions of minerals; and the appearance of new grain sizes, textures, and/or morphologies. The concept of mineral evolution thus places mineralogy in a dynamic historical context, in which different mineral species and mineralogical characteristics arose at different stages of planetary history as new modes of mineral paragenesis came into play. However, the initial presentation of this framework by Hazen et al. (2008) did not examine any one group of minerals in detail. Here we consider the important case of the evolution of phyllosilicate clay minerals, which, possibly more than any other mineral groups, exemplify the connections among the geosphere, hydrosphere, and biosphere (Elmore 2009).

It is likely that no phyllosilicate clay minerals were present in the pre-solar molecular cloud, which contained approximately a dozen micro- and nanoscale refractory “ur-minerals” (Hazen

et al. 2008). Yet, although clay minerals were absent during the initial high-temperature stages of planet formation, they now represent an important component of the near-surface crustal environment of Earth, Mars, and the parent bodies of carbonaceous chondrite meteorites. They also represent perhaps the most important class of minerals with which mankind interacts on a daily basis. Therefore, understanding the evolution of clay minerals as products of physical, chemical, and biological alteration processes is critical for understanding the mineralogical history of Earth and other worlds. Indeed, clay minerals provide a revealing case study for Earth's changing mineralogy through time for at least six reasons: (1) clay minerals first appeared in the early stages of planetary accretion and have been ubiquitous near-surface phases throughout our planet's history; (2) the 10 groups and more than 50 species of phyllosilicate clay minerals officially recognized by the International Mineralogical Association arise through varied paragenetic modes that parallel changing near-surface conditions and processes; (3) all of the principal clay mineral structure types are compositionally adaptable with diverse cations in tetrahedral, octahedral, and interlayer sites. Therefore, major, minor, and trace elements are likely to have varied systematically through time and thus reflect changing near-surface conditions, including compositions of parent rocks, solution chemistry, and redox state; (4) clay minerals exemplify mineralogical feedback mechanisms: for example, some clay minerals strongly interact with organic molecules, so sedimentary burial of clay minerals can sequester reduced carbon and thus enhance atmospheric oxidation (e.g., Berner 2004), which in turn affects the nature and rate of clay mineral formation; (5) clay minerals have played a significant

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TABLE 1. Clay mineral evolution

Stage	New clay minerals ¹	Age (Ga)	~No. of species
1. Chondrites; nebular processes	Primary high-T condensates; no clay minerals	>4.56 Ga	60
2. Aqueous alteration of C chondrites	Primarily Mg-Fe ²⁺ species: 8–10, 12–14, 34, 39, 46	>4.56 to 4.55 Ga	250
3. Earliest Hadean Earth; alteration of ultramafic and basaltic crust	Serpentinization and seafloor alteration dominate: 1, 2, 4, 5, 7, 11, 16, 17, 22, 24, 25, 27, 33, 35, 40, 50	<4.55 Ga	420
4. Formation of granitoids and pegmatites	Saprolites from granites/rare pegmatite clays: 3, 21, 31, 43, 44, 51, 55, 56	uncertain, >3.5 Ga	~1000
5. Initiation of plate tectonics	Metamorphic clay minerals from tectonic facies: 47, 49, 52	uncertain, >3.0 Ga	~1500
6. Origin of life; chemolithoautotrophs	Chemical weathering of terrestrial environments: 19, 23	>3.6 to 2.5 Ga	~1500
7. Great oxidation event	Clay minerals from oxidation reactions: 6, 18, 20, 26, 32, 36–38, 41, 42, 45, 53, 54	2.5 to 1.9 Ga	>4000
8. Intermediate ocean	No new clay minerals; global sedimentation/widespread clay deposition	1.9 to 1.0 Ga	>4000
9. Snowball Earth/hothouse cycles	No new clay minerals; episodic clay mineral production	1.0 to 0.542 Ga	>4000
10. Rise of the terrestrial biosphere	Increased biogenic clay mineral production: 15, 28–30, 48	0.542 Ga to present	>4800

Notes: Ten stages of Earth's mineral evolution saw changing rates and diversity of clay mineral formation. Note that the timings of some of these stages overlap, and several stages continue into the present (adapted from Hazen et al. 2008; Elmore 2009). Cumulative species refers to the total number of mineral species present, not just clay minerals.

¹ See Table 2, column 1 for clay mineral number key.

role in the mineralogy of Mars, and they hold the potential to reveal details of the evolution of the near-surface martian environment; and (6) clay minerals highlight the co-evolution of Earth's geosphere and biosphere. Clays likely played critical roles in the origin of life, and life has played a dramatic role in the production of near-surface clay minerals. Note, however, that despite fascinating "clay origin of life" speculations by Cairns-Smith and coworkers, who posit that the first life forms were self-replicating and evolving clay mineral assemblages (Cairns-Smith and Hartman 1986; Cairns-Smith 2005; Schumann et al. 2012), observational evidence does not support the contention that clay minerals "evolve" from prior generations by common descent. Mineral evolution instead refers to the tendency of Earth's near-surface environment to display congruent complexification, and thus to parallel other evolving natural and technological systems (Hazen and Eldredge 2010).

Understanding Earth's changing near-surface clay mineralogy through deep time is complicated by the fact that most of Earth's early clay mineral record has been erased as a result of burial, tectonic activity, alteration, and erosion. In this respect, the study of clay mineral evolution presents challenges related to preservational bias that are much more extreme than those of some other mineral systems (Hazen et al. 2009, 2012, 2013; Grew and Hazen 2009, 2010a, 2010b, 2013; Golden et al. 2013). Nevertheless, much about the 4.5 billion year evolutionary history of clays can be inferred from observations of the rock record and studies of modern clay-forming processes.

Our objective is to trace the changing diversity, distribution, and environments of clay minerals from planetary accretion to the modern terrestrial biological era through 10 stages of mineral evolution (Table 1). We focus on several overarching questions: What were Earth's first clay minerals? When and how did they form? What new clay minerals were associated with the formation of granitoids, the initiation of plate tectonics, and the Great Oxidation Event? How have the rates of clay mineral production changed over geological time? How does the distribution of clay minerals in the terrestrial environment reflect changes in atmospheric composition? And what effects have biological organisms had on clay mineral production? To address these questions we examine roles of the principal paragenetic modes of clay mineral formation through 10 stages of Earth's mineral evolution.

CLAY MINERAL GROUPS AND SPECIES

Our survey of clay mineral evolution focuses on predominantly fine-grained (<2 μm) layered phyllosilicate minerals (Guggenheim and Martin 1995), including 56 clay mineral species that have been approved by the International Mineralogical Association based on criteria of composition and structure [see the RRUFF database (<http://rruff.info>; Downs 2006); Table 2]. The phyllosilicate clay minerals considered here include the kaolin and serpentine groups, the talc and pyrophyllite groups, the expandable smectite and vermiculite groups, the illite group, the chlorite group, and the sepiolite-palygorskite group. Although locally important, we do not systematically treat interstratified clay mineral assemblages, or layered oxide hydroxides, or other phases (including amorphous phases) closely associated with phyllosilicate clay minerals (Table 3).

Despite the official status of species listed in Table 2, ambiguous terminology complicates the study of clay minerals, which can be defined in terms of particle size, major-element chemistry, and/or structure. Natural "clay" samples are commonly complex mixtures of both layered phyllosilicates and other oxide-hydroxide phases, such as gibbsite [$\text{Al}(\text{OH})_3$], brucite [$\text{Mg}(\text{OH})_2$], allophane [$\text{Al}_2\text{O}_3(\text{SiO}_2)_{1.3-2.0} \cdot 2.5-3.0\text{H}_2\text{O}$], imogolite [$\text{Al}_2\text{SiO}_5(\text{OH})_4$], and nanocrystalline iron oxide-hydroxides. Many clay minerals also lack the three-dimensional order of most mineral species, which complicates accurate description and understanding of their crystal structures. In addition, natural clay accumulations rarely display mono-mineralic properties. Complex solid solutions among multiple end-members and interstratification in fine-grained phyllosilicates make unambiguous identification of valid species difficult, whereas some oft-cited clay-type materials such as attapulgite, bauxite, bentonite, phengite, and steatite are not recognized as valid mineral species (Table 3). Furthermore, the nomenclature approved by the Association Internationale pour l'Étude des Argiles (AIPEA; Guggenheim et al. 2006, 2007) for clay mineral groups and species is not entirely consistent with that of the IMA.

The kaolin group

The kaolin group includes the kaolinite, dickite, nacrite, and halloysite-7 Å polymorphs of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, which are dioctahedral 1:1 clay minerals in which a single octahedral sheet is bonded to a single tetrahedral sheet to yield a ~ 7 Å *c*-axis repeat (Keller

1970; Joussein et al. 2005). Halloysite $[Al_2Si_2O_5(OH)_4 \cdot nH_2O; 0 < n < 2]$ occurs as a solid-solution series between halloysite-7 Å with $n = 0$ and halloysite-10 Å with $n = 2$ (Bailey 1980; Guggenheim and Eggleton 1988; Joussein et al. 2005). Hisingerite $[(Fe^{3+})_2Si_2O_5(OH)_4 \cdot 2H_2O]$ is the ferric iron isomorph of halloysite-10 Å (Eggleton and Tilley 1998).

The serpentine group

Serpentine group minerals, including several species encompassed by the general formula $[(Mg, Ni^{2+}, Fe^{2+}, Mn^{2+}, Zn, Fe^{3+}, Al)_3 (Al, Fe^{3+}, Si)_2 O_5 (OH)_4]$, are trioctahedral 1:1 layer phyllosilicates with a ~ 7 -Å c -axis repeat. The serpentine group most often occurs in grain sizes larger than those of true clay minerals (i.e., > 2 μm). However, we include it here because of its close structural similarity to the dioctahedral kaolin group and because the serpentine group does include some clay-sized occurrences (including a very early clay-sized fraction in some altered chondrites from stage 2 of mineral evolution; Weaver 1989; Brearley and Jones 1998; Zega et al. 2003). The serpentine group includes at least 15 recognized mineral species, including several Mn, Ni, and Zn species that form in altered ore deposits (Table 2). Note, however, that (as with most clay mineral groups) many of these “species” exhibit complete solid solution among more than a dozen chemical elements and that strict species identification is often difficult.

The talc and pyrophyllite group

The trioctahedral 2:1 talc group, including talc $[Mg_3Si_4O_{10}(OH)_2]$ and several isomorphs, are clay minerals with the 10 Å mica-like tetrahedral and octahedral layer arrangement, but without interlayer cations owing to their lack of a layer charge. Pyrophyllite $[Al_2Si_4O_{10}(OH)_2]$ is the dioctahedral 2:1 phyllosilicate with no layer charge.

The smectite and vermiculite group

Smectites and vermiculites are expandable 2:1 clay minerals, containing variable amounts of interlayer cations and H_2O molecules (Bailey 1984; Severmann et al. 2004; Güven 2009). They include at least 11 IMA-approved species (Table 2), including the important minerals montmorillonite $[(Na, K, \frac{1}{2}Ca)_{0.5}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O]$ (the primary constituent of bentonite), beidellite $[(K, Na, \frac{1}{2}Ca)_{0.3}Al_2(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O]$, and nontronite $[Na_{0.3}Fe_3^{3+}(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O]$. These phases expand in the presence of water by hydration of their interlayer cations, and their interlayer cations are readily exchangeable. The weak interlayer bonding leads to poorly ordered crystals, and turbostratic stacking (Bailey 1984) results in broad X-ray diffraction features that complicate identification. Both smectite- and vermiculite-group minerals are generally so disordered that it is not possible to define a three-dimensional crystal structure (Grim 1968; Mering 1975; Brindley 1980).

The illite group

Illite $\{[K_{0.6}(H_3O)_{0.4}]Al_{1.3}Mg_{0.3}Fe_{0.1}^{2+}Si_{3.5}O_{10}(OH)_2 \cdot (H_2O)\}$ and glauconite $\{[K, Na, (H_3O)^+]_x(Mg, Fe^{2+}, Al, Fe^{3+})_2(Al, Si)_4O_{10}(OH)_2 \cdot nH_2O\}$ are 10 Å dioctahedral, non-expandable “hydrated micas” that can incorporate variable amounts of H_2O molecules with interlayer cations, such as sodium and potassium. Illite is com-

monly found interstratified with other clay minerals, most often with smectite. Note that the official IMA status of illite and glauconite is pending, and phengite $[K(Mg, Al)_2(Si, Al)_4O_{10}(OH)_2]$, which was once included in this group, has been discredited as a distinct mineral species. Note, however, that “phengite” is still commonly cited as a morphologically distinct metamorphic modification of illite.

The chlorite group

All species of the chlorite group, with general formula $[(Li, Mg, Ni, Zn, Cr, Fe^{2+}, Mn^{2+}, Fe^{3+}, Al)_{5-6}(Si, Al, Fe^{3+}, B)_6O_{10}(OH)_8]$, have a 14-Å 2:1:1 layer structure; that is they have a 2:1 layer structure with an additional octahedral sheet in the interlayer region. As a result, it is possible to have four structural variants of chlorites, with either a di- or trioctahedral sheet in both the 2:1 layer and the interlayer octahedral sheet. Trioctahedral ferromagnesian chlorite-group minerals, including clinochlore $[Mg_6Si_4O_{10}(OH)_8]$ and chamosite $[(Fe^{2+}, Mg, Al, Fe^{3+})_6(Si, Al)_4O_{10}(OH)_8]$, are the most common species and are found in low-grade metamorphic rocks as alteration products of pyroxenes, amphiboles, biotite, and garnet (Alt et al. 1995; Klein and Hurlbut 1999; Alt and Bach 2001).

The palygorskite and sepiolite group

Palygorskite and sepiolite [ideally $(Mg, Al)_2Si_4O_{10}(OH) \cdot 4H_2O$ and $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, respectively] are distinctive fibrous chain-structured clay minerals that are relatively uncommon in nature (Bailey 1988a). Minerals of these groups differ by incorporating two (in palygorskite) and three (in sepiolite) pyroxene-like chains. The tetrahedral layers can be considered to be continuous, although they flip every two or three chain widths.

Related “clay-like” (non-phyllosilicate) materials

Although not the main focus of this article, several accessory non-phyllosilicate “clay-like” minerals are important in the context of clay mineral evolution. The amorphous phases allophane, imogolite, and neotocite $[(Mn^{2+}, Fe^{2+})SiO_3 \cdot H_2O]$, all of which are found in soils associated with the weathering of volcanic ashes and glasses (Bates 1962; Dudas and Harward 1975; Su and Harsh 1998; Dubroeuq et al. 1998; Churchman 2000), possess disordered structures (Wada 1989). Gibbsite, which is commonly found in highly weathered environments such as laterites, and brucite, which occurs in altered or weathered ultramafic rocks and in serpentine-brucite-magnetite assemblages during serpentinization, are common layered hydroxides with ~ 4 Å layer thickness. These hydroxides are similar to the “octahedral sheet” components of phyllosilicates. Nanophase iron oxide-hydroxides, also commonly associated with clay mineral assemblages, are extremely redox sensitive and thus important in Earth’s mineral evolution.

Different sheet arrangements, random stacking of interstratified hydroxide and phyllosilicate layers, variable chemical substitutions, variable hydration states, and numerous other defects complicate the description of natural clay minerals and clay assemblages and often blur a precise formal definition of what constitutes a clay mineral species. In particular, interstratified clays, for example illite/smectite, are ubiquitous in diagenetic sequences in pelitic rocks and are often found in soils and rego-

TABLE 2. Ten clay mineral groups and 56 phyllosilicate clay mineral species (as listed on <http://rruff.info/ima/>) cited in text, with their distributions through Earth history, paragenetic modes, and precursor minerals

No. group/Species name	Ideal formula	Stages ¹	Paragenetic modes ² ; Precursor minerals	References ³
Kaolinite group (7 Å dioctahedral 1:1 layer structure)				
1. Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	(3),4 4 4 4 10	HYDR—feldspars, feldspathoids, muscovite, biotite WEAT—granite, aluminosilicates DEHY—halloysite-10 Å AUTH—detrital sediments SOIL,BIOL—illite, vermiculite	1–3 4, 5 6 4 7–9
2. Dickite	Al ₂ Si ₂ O ₅ (OH) ₄	(3),4 (3),4	HYDR—aluminosilicates; DIAG—kaolinite AUTH—sediments	10 10
3. Nacrite	Al ₂ Si ₂ O ₅ (OH) ₄	4	HYDR—aluminosilicates	10
4. Halloysite-7Å	Al ₂ Si ₂ O ₅ (OH) ₄	3 4 4	HYDR—aluminosilicates in mafic and ultramafic rocks WEAT—felsic igneous and metamorphic rocks DEHY—halloysite-10 Å above 110 °C	1, 11, 12 13–18 19
5. Halloysite-10Å	Al ₂ Si ₂ O ₅ (OH) ₄ ·2H ₂ O	3 3,10	HYDR—aluminosilicates in mafic and ultramafic rocks WEAT,SOIL—mafic and ultramafic rocks	1,11,12 13–18
6. Hisingerite	(Fe ³⁺) ₂ Si ₂ O ₅ (OH) ₄ ·2H ₂ O	7,10	OXID,WEAT—Fe silicates or sulfides	20
Serpentine group (7 Å trioctahedral 1:1 layer structure)				
7. Amesite	Mg ₂ Al(SiAl)O ₅ (OH) ₄	(3),(5)	RMET,HYDR—Al-Mg-rich rocks	10
8. Antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄	(2) 3 6	ACHN—C chondrites HYDR,SERP—ultramafics CMET—dolostone transformed to forsterite	21 22 10
9. Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	(2) 3	ACHN—CM chondrites HYDR,SERP—mafic and ultramafic rocks	21 22
10. Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	(2) 3	ACHN—C chondrites HYDR,SERP—olivine, orthopyroxene	21 10,22
11. Caryopilite	(Mn ²⁺) ₃ Si ₂ O ₅ (OH) ₄	(3),(5) (6)	CMET,HYDR—Mn minerals, such as rhodonite WEAT—Mn deposits	23 23
12. Berthierine	(Fe ²⁺ ,Fe ³⁺ ,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	(2) (3),4 10	ACHN—CM chondrites AUTH—banded iron formations, marine sediments LATR,BIOL—soils	21 24 24
13. Cronstedtite	(Fe ²⁺ ,Fe ³⁺) ₃ (Si,Fe ³⁺) ₂ O ₅ (OH) ₄	(2) 7	ACHN—CM chondrites OXID,HYDR—ore veins	21 10
14. Greenalite	(Fe ²⁺ ,Fe ³⁺) ₂₋₃ Si ₂ O ₅ (OH) ₄	(2) (6),7	ACHN—CM chondrites AUTH—banded iron formations	21 25
15. Odinite	(Fe ³⁺ ,Mg,Al,Fe ²⁺) ₂₋₃ (Si,Al) ₂ O ₅ (OH) ₄	(10)	BIOL,AUTH—tropical reefs	26
16. Népouite	Ni ₃ Si ₂ O ₅ (OH) ₄	(3) (10)	HYDR,SERP—Ni-rich ultramafic rocks LATR—Ni laterites	27 27
17. Pecoraite	Ni ₃ Si ₂ O ₅ (OH) ₄	(3) (4)	HYDR—Ni-rich ultramafic rocks WEAT—millerite (NiS)	28 28
18. Brindleyite	(Ni,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	(7)	OXID,WEAT—ultramafic rocks, bauxite deposits	29
19. Kellyite	(Mn ²⁺ ,Mg,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	6	HYDR,WEAT—Mn-bearing carbonates and basic rocks	30
20. Fraipontite	(Zn,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	(7)	OXID,HYDR,WEAT—Zn-bearing rocks	31
21. Manandonite	Li ₂ Al ₄ (Si ₂ AlB)O ₁₀ (OH) ₈	(4)	HYDR,WEAT—complex Li-B pegmatites	32
Talc group (10 Å trioctahedral, non-expandable 2:1 layer structure; no interlayer cations)				
22. Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	3 (3),4 5	HYDR—olivines and non-Al pyroxenes WEAT—ultramafic RMET—Mg-rich rocks	7,10,33 1,34 1
23. Minnesotaite	(Fe ²⁺) ₃ Si ₄ O ₁₀ (OH) ₂	(6),7	RMET—banded iron formations	10,35
24. Willemseite	Ni ₃ Si ₄ O ₁₀ (OH) ₂	(3)	HYDR—Ni-bearing igneous rocks	36
Pyrophyllite group (10 Å dioctahedral, non-expandable 2:1 layer structure; no interlayer cations)				
25. Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	(3),4 (5)	HYDR—feldspar RMET—kyanite, Al-pyroxene	10 10
26. Ferripyrophyllite	Fe ₂ ³⁺ Si ₂ O ₁₀ (OH) ₂	(7)	OXID,HYDR—iron formations	37
Palygorskite-sepiolite group (10 Å di- and trioctahedral, expandable 2:1 layer structure; usually in fibrous habit)				
27. Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂ ·6H ₂ O	3 4	SERP—mafic rocks AUTH—alkaline saline waters in arid environments	10,38 10
28. Loughlinite	Na ₂ Mg ₂ Si ₆ O ₁₆ ·8H ₂ O	(10)	RMET—dolomitic shale	39
29. Falcondoite	Ni ₄ Si ₆ O ₁₅ (OH) ₂ ·6H ₂ O	(10)	LATR—serpentinized Ni-rich harzburgite	40
30. Palygorskite	(Mg,Al) ₂ Si ₄ O ₁₀ (OH) ₂ ·4H ₂ O	10	SOIL—Mg silicates	10,38
31. Yofortierite	(Mn ²⁺ ,Mg,Fe ³⁺) ₂ Si ₄ O ₂₀ (OH,H ₂ O) ₂ ·7H ₂ O	(4)	HYDR—pegmatite in nepheline syenite	41
32. Tapersuatsiaite	NaFe ₃ ³⁺ Si ₄ O ₂₀ (OH) ₂ ·4H ₂ O	(7)	OXID,HYDR—sodalite-nepheline syenite pegmatite	42
Smectite and vermiculite groups (10 Å di- and trioctahedral, expandable 2:1 layer structure; no interlayer cations)				
33. Vermiculite	Mg _{0.7} (Mg,Fe ³⁺ ,Al) ₆ (Si,Al) ₈ O ₂₀ (OH) ₄ ·8H ₂ O	(3),4 4 (5)	HYDR,WEAT—Mg micas, muscovite SOIL—clay minerals RMET—limestone	1,10,33,43–48 45,46 10
34. Saponite	(Ca,Na) _{0.3} (Mg,Fe ²⁺) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4H ₂ O	(2) 3	ACHN—CAIs, matrix, and chondrules in chondrites HYDR,SERP—basalt, skarns, amphibolites	21 33,48–50
35. Ferrosaponite	Ca _{0.3} (Fe ²⁺ ,Mg,Fe ³⁺) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4H ₂ O	(3)	HYDR—basalt	49,51
36. Sauconite	Na _{0.3} Zn ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4H ₂ O	(7)	OXID,HYDR—Zn ores	52
37. Zincsilite	Zn ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4H ₂ O	(7)	OXID, HYDR—Zn ores	53
38. Yakhontovite	(Ca,Na,K) _{0.2} (Cu,Fe,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·3H ₂ O	(7)	OXID,WEAT—Cu sulfide ore	54

(continued on next page)

TABLE 2.—CONTINUED

No. group/Species name	Ideal formula	Stages ¹	Paragenetic modes ² ; Precursor minerals	References ³
39. Montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O	2	ACHN—CAls and matrix in chondrites	21
		3	HYDR—volcanic and intrusive rocks	1,2,10,55,56
		3	WEAT—volcanic tuff and ash	1,2,10,57,58
40. Beidellite	(Na,Ca) _{0.3} Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ ·nH ₂ O	3	HYDR—volcanics (bentonites)	10,43,56,59,60
		4	SOIL—mafic rocks	10,59
		(5)	HYDR—porphyry Cu	10,59
41. Nontronite	Na _{0.3} Fe ²⁺ (Si,Al) ₄ O ₁₀ (OH) ₂ ·nH ₂ O	7	OXID,WEAT—basalt and ultramafic rocks	10,61,62
		7	OXID, HYDR—mafic rocks	10,55,56,63,64
		(7)	CMET—limestone	10
		7	OXID,AUTH—marine sediments	10,58,65
42. Volkonskoite	Ca _{0.3} (Cr,Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4(H ₂ O)	(7),(10)	OXID,WEAT—serpentinites	66
		(10)	AUTH,BIOL—sediments with organics	66
43. Swinefordite	Ca _{0.2} (Li,Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ (OH,F) ₂ ·nH ₂ O	(4)	AUTH—spodumene in pegmatites	67
Illite group (10 Å dioctahedral, 2:1 layer structure; with interlayer cations)				
44. Illite ⁴	[K _{0.6} (H ₃ O) _{0.4} Al _{1.3} Mg _{0.3} Fe _{0.1} Si _{3.5} O ₁₀ (OH) ₂ ·(H ₂ O)]	4	AUTH,WEAT—feldspar	1,2,10,43,44,68
		4	HYDR—muscovite-phengite	1,2,10,12,33,68
		4	SOIL—smectite	1,10,69
45. Glauconite ⁴	(K,Na)(Fe ³⁺ ,Al,Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂	7	DIAG,RDUC—biotite in shallow water	10,70
		7,10	BIOL—biotite alteration with organics	71
Chlorite group (14 Å di- and trioctahedral, 2:1:1 layer structure)				
46. Clinocllore	Mg ₅ Al(Si ₃ O ₁₀)(OH) ₈	(2)	ACHN—chondrite	21
		3	HYDR—amphibole, pyroxene, biotite	10
		5	RMET—chlorite schist, marble, amphibolite, ultramafic	10,22,72
47. Chamosite	(Fe ²⁺ ,Mg,Al,Fe ³⁺) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	5	RMET—Fe, Mg silicates	22,72
		7,10	AUTH,RDUC—sedimentary ironstones and organics	10
48. Orthochamosite	Fe ²⁺ Al(Si,Al) ₄ O ₁₀ (OH) ₈	(10)	LATR—olivine basalt	73
49. Pennantite	(Mn ²⁺ ,Al) ₂ (Si,Al) ₄ O ₁₀ (OH) ₈	(5)	RMET—Fe, Mg silicates	22,72
		(7)	HYDR—Mn deposits	74
50. Nimite	(Ni,Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	(3)	HYDR,SERP—Ultramafic Ni deposits	75
		(5)	RMET—Fe, Mg silicates	22,72
51. Donbassite	Al ₂ (Si ₃ Al) ₂ O ₁₀ (OH) ₂ ·Al _{2.33} (OH) ₈	(4)	AUTH—Al-rich sediments	76
		(5)	HYDR—andalusite	76
52. Sudoite	Mg ₂ Al ₃ (Si ₃ Al) ₂ O ₁₀ (OH) ₈	(6),(7)	OXID,HYDR—hematite ore	77
		(5)	AUTH—aeolian sandstones	78
(5)	RMET—low-grade assemblages	79		
53. Gonyerite	Mn ²⁺ Fe ³⁺ (Si ₃ Fe ³⁺)O ₁₀ (OH) ₈	(7)	OXID,HYDR—Mn deposits, skarns	80
54. Baileychlorite	(Zn,Fe ²⁺ ,Al,Mg) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	(7)	OXID;WEAT—Zn ores, skarns	81
55. Cookeite	(Al,Li) ₂ Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₈	(4)	HYDR—tourmaline and lepidolite in pegmatites	10
56. Borocookeite	LiAl ₄ (Si ₃ B)O ₁₀ (OH) ₈	(4)	HYDR; tourmaline in pegmatites	82

Note: Modified and expanded from Hower and Mowatt (1966), Brindley (1980), Bailey (1980, 1988a), Srodon (1984), Moore and Reynolds (1997), and web databases, including <http://www.mindat.org> and <http://webmineral.com/data>.

¹ See Table 1 for the list of 10 stages of mineral evolution. Parentheses indicate relatively minor clay mineral production during that stage.

² Paragenetic modes include: ACHN = achondrite alteration; AUTH = authigenesis; BIOL = biological mediated; CMET = contact metamorphism; DEHY = dehydration; DIAG = diagenesis; HYDR = hydrothermal alteration; LATR = laterite formation; META = regional metamorphism; OXID = oxidative weathering; RDUC = reduction; RMET = regional metamorphism; SERP = serpentinization; SOIL = Phanerozoic soil formation; WEAT = subaerial weathering

³ References: 1. Weaver (1989); 2. Berner (1971); 3. Stoch and Sikora (1976); 4. Keller (1970); 5. Meunier (1980); 6. Giese (1988); 7. Newman (1987); 8. Calvert et al. (1980); 9. Siffert (1978); 10. Deer et al. (1962); 11. Joussein et al. (2005); 12. Maksimović and Brindley (1980); 13. Huang (1974); 14. Dudas and Harward (1975); 15. Romero et al. (1992); 16. Ziegler et al. (2003); 17. Churchman (2000); 18. Brindley and Goodyear (1948); 19. Tazaki (2005); 20. Eggleton and Tilley (1998); 21. Brearley and Jones (1998); 22. Alt and Bach (2001); 23. Peacor and Essene (1980); 24. Brindley (1982); 25. Jolliffe (1935); 26. Bailey (1988b); 27. Brindley and Wan (1975); 28. Milton et al. (1983); 29. Maksimović and Bish (1978); 30. Peacor et al. (1974); 31. Franolet and Bourguignon (1975); 32. Ranoroosa et al. (1989); 33. Velde (1985); 34. Whitney and Eberl (1982); 35. Gruner (1944); 36. De Waal (1970a); 37. Badaut et al. (1992); 38. Bailey (1988a); 39. Fahey et al. (1960); 40. Springer (1976); 41. Perrault et al. (1975); 42. Karup-Moller and Petersen (1984); 43. Meunier and Velde (1979); 44. Velde and Weir (1979); 45. Roy and Romo (1957); 46. Jackson et al. (1952); 47. Johnson (1964); 48. Caillaud et al. (2006); 49. Nozaka et al. (2008); 50. Ames and Sands (1958); 51. Chukanov et al. (2003); 52. Ross (1946); 53. Smol'yaninova et al. (1961); 54. Postnikova et al. (1991); 55. Singer and Stoffers (1987); 56. Linares (1987); 57. Christidis and Huff (2009); 58. Harder (1972); 59. Weir and Greene-Kelly (1962); 60. Proust and Velde (1978); 61. Harder (1976); 62. Ducloux et al. (1976); 63. Murnane and Clague (1983); 64. Alt (1988); 65. Bischoff (1972); 66. Khoury et al. (1984); 67. Tien et al. (1975); 68. Hower and Mowatt (1966); 69. Kim et al. (2004); 70. Meunier and El Albani (2007); 71. Odin (1988); 72. Alt et al. (1995); 73. Novák et al. (1957); 74. Smith et al. (1946); 75. De Waal (1970b); 76. Lazerenko (1941); 77. Eggleton and Bailey (1967); 78. von Engelhardt et al. (1962); 79. Kramm (1980); 80. Frondel (1955); 81. Rule and Radke (1988); 82. Zagorsky et al. (2003).

⁴ IMA status uncertain.

liths. In addition, soil smectites also commonly contain partially developed hydroxide interlayers, essentially forming material intermediate between smectite and chlorite.

CLAY MINERAL EVOLUTION

Hazen et al. (2008) described three eras of Earth's mineral evolution, further divided into 10 partly overlapping stages (Table 1). The first era of planetary accretion is represented by ~60 primary condensate minerals identified in primitive chondrite meteorites (stage 1), and the much more diverse suite of minerals

produced by alteration and differentiation in achondrites and other meteorites (stage 2).

The second era of crust and mantle reworking is represented by three stages of mineral evolution. For the purposes of clay mineral evolution, we define stage 3 as the earliest part of the Hadean Eon following Earth's differentiation at ~4.5 Ga—a time characterized by the formation and alteration of an ultramafic and basaltic lithospheric veneer, as well as the first (presumably shallow) hydrosphere. Stage 4, which may also have begun during the Hadean Eon, commenced with the production of granitoids and

TABLE 3. IMA-approved and provisional clay-like minerals cited in text, selected widely cited but not IMA-approved clay minerals, and related clay-like materials

IMA-approved mixed-layer clay minerals		
Corrensite	$(Ca,Na,K)_{1-x}(Mg,Fe,Al)_9(Si,Al)_8O_{20}(OH)_{10}\cdot nH_2O$	Interstratified trioctahedral chlorite with trioctahedral vermiculite ("corrensite-1") or with trioctahedral smectite ("corrensite-2")
Rectorite	$(Na,Ca)Al_4(Si,Al)_6O_{20}(OH)_4\cdot 2H_2O$	Interstratified dioctahedral mica and smectite; alteration of K-feldspar or muscovite
Dozyite	$Mg_7Al_2(Si_4Al_2)O_{15}(OH)_{12}$	Interstratified serpentine and chlorite; altered skarn
Tosudite	$Na_{0.5}(Al,Mg)_6(Si,Al)_8O_{20}(OH)_{12}\cdot 5H_2O$	Interstratified dioctahedral chlorite and smectite; hydrothermal alteration of tuffs, andesites
Kulkeite	$Na_{0.3}Mg_8Al(Si,Al)_8O_{20}(OH)_{10}$	Interstratified trioctahedral chlorite and talc; meta-evaporite sequence
Aliettite	$Ca_{0.2}Mg_6(Si,Al)_8O_{20}(OH)_4\cdot 4H_2O$	Interstratified talc and saponite; occurs in low- <i>T</i> ancient lake sediments; low-grade Mg-rich metamorphic rocks
Hydrobiotite	$K(Mg,Fe^{2+})_6(Si,Al)_8O_{20}(OH)_4\cdot nH_2O$	Interstratified biotite and vermiculite; sedimentary environments
Lunijianlaite	$Li_{0.7}Al_{6.2}(Si_7Al)_{20}(OH)_4O_{10}$	Interstratified cookeite and pyrophyllite; pegmatite alteration
Saliotite	$(Li,Na)Al_3(Si_3Al)O_{10}(OH)_5$	Interstratified cookeite and paragonite; pegmatite alteration
Selected oxide-hydroxides		
Boehmite	AlO(OH)	
Brucite	Mg(OH) ₂	
Diaspore	AlO(OH)	
Gibbsite	Al(OH) ₃	
Amorphous clay-related phases		
Allophane	$Al_2O_3(SiO_2)_{1.3-2.0}\cdot 2.5-3.0H_2O$	Weathering of volcanic ash; hydrothermal alteration of feldspar
Imogolite	$Al_2SiO_5(OH)_4$	Soils derived from volcanic ash
Neotocite	$(Mn^{2+},Fe^{2+})SiO_3\cdot H_2O$	Alteration of Mn-bearing sediments
Clay minerals widely cited but not approved by the IMA		
Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$	Discredited vermiculite group; hot springs alteration of volcanic tuff
Stevensite	$(Ca_{0.5},Na)_2Mg_2Si_4O_{10}(OH)_2$	Discredited vermiculite group; hydrothermal replacement of pectolite
Phengite	$K(Mg,Al)_2(Si,Al)_4O_{10}(OH)_2$	Discredited illite group; equivalent to fine-grained muscovite-celadonite
Kerolite	$(Mg,Ni)_3Si_4O_{10}(OH)_2\cdot H_2O$	Discredited talc group; lateritic soils
Unofficial clay-related terms, including clay rocks and commonly used designations for clay-like substances		
Attapulgite	A soil rich in smectite and palagorskite; mined in southern U.S. as binder for paints and numerous other applications	
Bauxite	An aluminum ore consisting primarily of the aluminum oxide-hydroxides gibbsite, diaspore and boehmite	
Bentonite	A clay rock formed principally of smectite, especially members of the montmorillonite-beidellite series	
Endellite	Synonym for halloysite-10 Å	
Hydrated halloysite	Synonym for halloysite-10 Å	
Kandites	The kaolinite group	
Laterite	A soil rich in Al and Fe, formed by extensive weathering and rich in clay minerals	
Pelite	Historic term for a fine-grained sedimentary rock rich in clay minerals	
Ripidolite	Historical name used for undetermined members of the chamosite-clinoclchlore series of chlorites	
Saprolite	A chemically weathered rock, typically rich in clay minerals	
Saprock	Fractured bedrock with alteration restricted to fracture zones; saprock lies below saprolite in a soil column	
Smectite-1	General term for dioctahedral (notably Al, Fe ³⁺) smectites	
Smectite-2	General term for trioctahedral (notably Mg, Fe ²⁺) smectites	
Steatite	Soapstone: a metamorphic rock rich in talc	

associated pegmatites by partial melting of stage 3 basalts, as well as by other granitization mechanisms. Stage 5 saw the activation of large-scale plate tectonic processes and fluid-rock interactions associated with subduction, convergent margin orogenesis, and exposure of deep metamorphic terrains. Note that the timings of stages 4 and 5 remain matters of considerable debate. Therefore, for the purposes of this review (and unlike the chronology suggested in Hazen et al. 2008) we do not assign specific time intervals to the earliest occurrences of granite formation and subduction.

The third era of Earth's mineral evolution focuses on the co-evolution of the geo- and biospheres. Prior to ~2.5 Ga microbial activity altered the Earth's surface in an anoxic environment (stage 6). The Great Oxidation Event (~2.4 to 2.2 Ga; stage 7) triggered the greatest episode of mineral diversification. The subsequent billion-year interval, an intriguing time known as the "intermediate ocean" (Anbar and Knoll 2002; stage 8), saw no obvious new modes of mineral paragenesis, although additional focus is needed on the apparent mineralogical diversification of this time period associated with the assembly of the Rodinian supercontinent (Grew and Hazen 2009, 2010a, 2013; Hazen et

al. 2012). Snowball Earth episodes of global glaciation (stage 9) served as preludes for increased atmospheric oxidation and the modern period of biomineralization (stage 10). In this section we explore how each of these three eras and 10 stages of mineral evolution are characterized in terms of the diversity, distributions, and environments of clay minerals.

The key to understanding the evolution of clay minerals lies in their varied modes of paragenesis. Clay minerals found at or near Earth's surface commonly arise from five partly overlapping processes, each of which was initiated at a different stage of Earth's mineral evolution (Table 1), and each of which introduced new clay species and rates of clay mineral production.

(1) Aqueous alteration. Aqueous alteration, including hydrothermal alteration and serpentinization, of pre-existing minerals has been an important clay-forming process since before Earth's accretion. Aqueous alteration within planetesimals produced the first minor quantities of clay minerals (stage 2). Subsequently, serpentinization of basalt and other mafic igneous lithologies (stage 3), coupled with seawater-basalt interactions, were the first volumetrically significant engine of clay mineralization. Aqueous

ous alteration of diverse igneous, sedimentary, and metamorphic lithologies has remained an important paragenetic mode for clay minerals throughout Earth history and is active today.

(2) Authigenesis. Direct precipitation of authigenic clays, especially from solution in marine sediments, alkaline lakes, and restricted marine environments [but also possibly from higher temperature magmatic fluids (Meunier et al. 2012)], represents a second, although volumetrically less important, mode of clay mineral paragenesis. Such a mechanism may have occurred on a significant scale early in Earth's history, as sediments accumulated on the basaltic floor of the Hadean Ocean. This accumulation of thick clay mineral-bearing marine sediments may have preceded the formation and erosion of the first granitic protocontinents (stage 4).

(3) Diagenesis. Clay minerals commonly form during diagenesis in sedimentary basins and during low-grade metamorphism (to greenschist facies) of varied lithologies, often including alteration of pre-existing clay minerals. Such clay-forming processes undoubtedly have operated since early in Earth's history. However, the surface manifestation of initially deep metamorphic terrains and the large-scale production of metamorphic clay minerals were probably not significant prior to the advent of plate tectonics (stage 5) and the exposure of deep crustal rocks through orogenesis. However, the detection of clay minerals associated with large ancient impact craters on Mars suggests that impact events may have played an important role in generating localized hydrothermal systems and excavating deep crustal rocks (Mustard et al. 2008; Carter et al. 2010; Ehlmann et al. 2011), and the same may have been true for early Earth (Pirajno 2009).

(4) Terrestrial weathering. Near-surface terrestrial weathering reactions are an important mode of clay mineral formation. Weathering must have produced minor amounts of clay minerals on early Earth, notably in the acidic environments of active volcanoes (stage 3) and on the earliest anoxic protocontinents (stage 4). However, production of clay minerals through oxidative weathering was not a significant factor until the Great Oxidation Event (stage 7), which not only saw the dramatically increased production of near-surface terrestrial clays, but also likely resulted in several new species of ferric iron clay minerals and extensive formation of lateritic soils.

(5) Biomediated clay mineralization. The rise of a terrestrial biosphere, most notably the advent of soil-forming microbes, fungi, and plants (stage 10), marked a dramatic transition in the diversity and rate of clay mineral production. Biological weathering in the Phanerozoic Eon may have increased the rate of terrestrial clay production by an order of magnitude (e.g., Ueshima and Tazaki 1998; Kim et al. 2004; Tazaki 2005), and it is likely that the compositional ranges, and possibly some specific clay mineral species formed as products of biological weathering, were distinct from those previously formed abiotically (e.g., Shelobolina et al. 2003; Stucki and Kostka 2006; Dong 2012).

Stage 1—Pre-accretionary processes (4.56 Ga)

About a dozen different micro- and nanoscale refractory “ur-minerals” have been identified in presolar grains (Brearley and Jones 1998; Nittler 2003; Table 2a in Hazen et al. 2008). Gravitational clumping of nebular material, primarily H, He, small molecular species, and presolar dust, led to star formation

and the resultant heating of the protoplanetary disk. This heating produced the primary refractory constituents of chondritic meteorites with their ~60 different known mineral phases [stage 1; Tables 2b–2e in Hazen et al. (2008)]. All minerals from these earliest stages of mineral diversification are high-temperature condensates and thus clay minerals are unlikely to have formed during (or prior to) these earliest pre-accretionary events in Earth's mineralogical history.

Stage 2—Post-accretionary processes (4.56–4.55 Ga)

As chondritic material accumulated through gravitational clumping into planetesimals, core-mantle differentiation and progressive aqueous, thermal, and shock alteration led to the ~250 different minerals that have been identified in meteorite samples (Brearley and Jones 1998; Krot et al. 2006; Brearley 2006; MacPherson 2004). Low-temperature (<100 °C) aqueous alteration of preexisting condensates produced the earliest known clay minerals, which are now found in various meteorites (Tables 1 and 2). Almost all types of carbonaceous chondrites, including CI, CM, CO, CV, and CR chondrites, experienced secondary aqueous alteration that produced clay minerals (Brearley and Jones 1998).

The matrices of many primitive CI chondrites are dominated (>50 to 60%) by clay minerals, including Mg-Fe serpentine-group minerals and saponite [(Ca,Na)_{0.3}(Mg,Fe²⁺)₃(Si,Al)₄O₁₀(OH)₂·4H₂O], with minor chlorite (Brearley and Prinz 1992). The Mg-Fe serpentine-group minerals cronstedtite [(Fe²⁺,Fe³⁺)₃(Si,Fe³⁺)₂O₅(OH)₄], chrysotile [Mg₃Si₂O₅(OH)₄], and greenalite [(Fe²⁺,Fe³⁺)₂₋₃Si₂O₅(OH)₄] and berthierine-group minerals also comprise a significant fraction of the matrix in CM chondrites, with reports of the smectite-group mineral saponite, as well (Brearley and Jones 1998; Zega et al. 2003). Saponite is also a common constituent of the altered matrix of CV and CR chondrites, and secondary alteration of Ca-Al inclusions (CAIs) in CV-type chondrites results in montmorillonite and possibly serpentine and saponite (Tomeoka and Buseck 1990). Clay mineral production may have been accelerated in the presence of oxalate and other polar organic molecules found in carbonaceous meteorites (Schumann et al. 2012).

In addition to clay minerals formed during aqueous alteration of chondrite meteorites, interplanetary dust particles also display a range of clay minerals formed by secondary alteration of ferromagnesian silicates (Reitmeijer 1998). Thus, at least 9 Mg- and/or Fe-bearing clay mineral species, most of them serpentines and smectites, were produced in the solar nebula, principally by aqueous alteration contemporaneously with Earth's accretion, and they are recorded from stage 2 (Table 1). Note that Reitmeijer et al. (2006) also propose that some clay-bearing assemblages might form under metastable eutectic conditions, whereas Meunier et al. (2012) invoke “magmatic precipitation” of clay minerals. However, other modes of clay mineral paragenesis, including authigenic formation in sediments, surface weathering and oxidation, or biologically mediated mineralization, would not have occurred during stage 2.

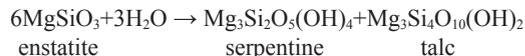
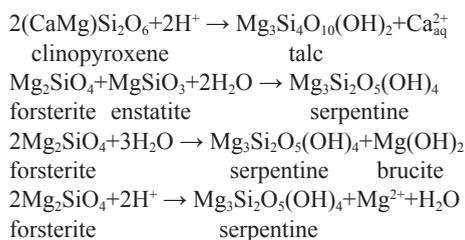
Stage 3—Earliest Hadean Earth (<4.55 Ga)

Stage 3 of Earth's mineral evolution was dominated by the production and subsequent alteration of near-surface ultramafic

and mafic rocks. Igneous processes, including volcanism and degassing, fractional crystallization, crystal settling, and assimilation reactions, led to the familiar Bowen's reaction series (Bowen 1928). On volatile-poor (i.e., essentially anhydrous in their near-surface environments) terrestrial bodies such as Mercury and the Moon, which likely only progressed through stage 3 of mineral evolution, clay minerals cannot represent volumetrically significant phases. [A possible exception might occur in hydrothermal zones beneath the shaded margins of ice-filled craters near the poles of these bodies (Lawrence et al. 2013).] However, on volatile-rich bodies such as Earth and Mars, as many as 420 mineral phases, including a potential suite of 25 clay minerals (Tables 1 and 2), may have been present in the near-surface environment from the earliest period, primarily as a result of aqueous alteration and low-temperature metamorphism of ultramafic and mafic lithologies (Hazen 2013). We estimate that 16 of these clay minerals appeared for the first time in stage 3 (Tables 1 and 2). Several clay minerals with presumed similar parageneses have now been detected in the ancient crust of Mars, which is thought to have formed during this time period.

This mineralogical diversification on Earth was halted when the crust and outer mantle were violently disrupted and melted by the Moon-forming impact event at ~4.55 Ga (Tonks and Melosh 1993; Ruzicka et al. 1999; Touboul et al. 2007). Immediately following that catastrophic event, Earth's near-surface mineralogy was reset as a consequence of igneous rock crystallization. Intense volcanism and associated mantle outgassing rapidly produced a water-rich near-surface environment, with globe-spanning shallow oceans probably forming prior to 4.4 Ga (Wilde et al. 2001). Aqueous low-temperature reactions, surface weathering, and hydrothermal alteration of the ultramafic and basaltic crust may have resulted in the extensive production of trioctahedral ferromagnesian clay minerals.

Earth's earliest rocks, including komatiites, peridotites, basalts, and other ultramafic and mafic volcanics (Arndt and Nisbet 1982; Rollinson 2007; Papineau 2010), were dominated by the Mg-Fe silicates olivine [(Mg,Fe)₂SiO₄], orthopyroxene [(Mg,Fe)SiO₃], and clinopyroxene [(Mg,Fe,Ca)SiO₃]. Hydrothermal alteration of these ferromagnesian minerals was initiated by the high solubility of Mg. Indeed, primary olivine and pyroxene are often completely altered, making it difficult to determine the initial compositions of some ancient ultramafic rocks. Mg-Fe silicates typically alter via serpentinization reactions (Schrenk et al. 2013) to trioctahedral ferromagnesian clays, including serpentine, talc, and chlorite, which were thus Earth's first volumetrically significant clay minerals. Typical clay-forming alteration reactions of olivine and pyroxenes (Deer et al. 1962; Harder 1976; Fontanaud and Meunier 1983; Newman 1987; Nozaka et al. 2008) include:



In addition to serpentinization reactions, interactions between basalt and seawater that lead to seafloor basalt weathering have been a major source of clay minerals throughout Earth history, as well as a significant source of dissolved ionic species in seawater (Scarfe and Smith 1977; Hajash and Archer 1980; Papavassiliou and Cosgrove 1981; Seyfried and Mottl 1982; Thompson 1983; Daughney et al. 2004). Weathering products commonly include dioctahedral and trioctahedral smectites, as well as poorly ordered smectite-chlorite mixed layerings.

Aqueous alteration of ferromagnesian minerals is often characterized by a sequence of clay minerals with decreasing Mg/Si; for example, olivine may be first serpentinized to antigorite, chrysotile, and lizardite [all forms of Mg₃Si₂O₅(OH)₄] and later be replaced by other clay minerals, including vermiculite [Mg_{0.7}(Mg,Fe³⁺,Al)₆(Si,Al)₈O₂₀(OH)₄·8H₂O], mixed-layer saponite-talc, and saponite (Velde 1985; Alt and Bach 2001; Blackman et al. 2006; Caillaud et al. 2006; Nozaka et al. 2008). Note that serpentinization is a significantly exothermic process for compositions more Mg-rich than Fo25 (Oze and Sharma 2006). Consequently, extensive Hadean clay mineralization likely represented a significant component of near-surface heat flow.

Ultramafic and mafic lithologies are also characterized by primary Ca and Al silicates, including amphiboles and plagioclase feldspars, which are subject to deep-sea weathering. The amphiboles tremolite [Ca₂Mg₅Si₈O₂₂(OH)₂], actinolite [Ca₂(Mg,Fe²⁺)₅Si₈O₂₂(OH)₂], and magnesiohornblende [Ca₂[Mg₄(Al,Fe³⁺)]Si₇AlO₂₂(OH)₂] commonly alter to clay minerals (Jayananda et al. 2008). Proust et al. (2006) observed that alteration of calcic amphibole produced a sequence of four clay minerals as a function of crystallization sites in a single amphibole crystal: (1) saponite; (2) montmorillonite; (3) interstratified kaolinite/smectite; and (4) halloysite. Thus, deposits with multiple coexisting clay mineral species can result from alteration of a single progenitor. Similarly, Garvie and Metcalfe (1997) report a vein occurrence of coexisting talc, saponite, and corrensite [(Ca,Na,K)_{1-x}(Mg,Fe,Al)₉(Si,Al)₈O₂₀(OH)₁₀·nH₂O], and Stakes and O'Neil (1982) found coexisting actinolite, smectite, vermiculite, talc, chlorite, saponite, and chlorite-smectite.

In addition to extensive serpentinization, diagenetic clay-forming processes may have been significant at this stage. The ocean floors, covered by fresh basalt with minimal sediment overburden and relatively high-heat flow, would have facilitated diagenetic production of saponite and perhaps nontronite. However, given the likely localized and volumetrically minimal deposits of Hadean marine sediments, the production of non-aluminous authigenic clay minerals may have been restricted. Anoxic, CO₂-rich surface weathering of volcanic islands that rose above the global Hadean ocean, with possible associated production of montmorillonite, saponite, and sepiolite, would have been similarly localized and volumetrically minor. Note also that in the absence of extensive felsic granitic lithologies (i.e., stage 4), Fe-Mg trioctahedral clay minerals would have volumetrically exceeded Al-Fe³⁺ dioctahedral clay minerals in anoxic environments.

The presence of an anoxic near-surface environment during

stage 3 would have affected the redox state of clay minerals. Ferrous iron would have dominated ferric iron, thereby further exaggerating the dominance of trioctahedral vs. dioctahedral clay species. Thus, saponite is likely to have been far more abundant than vermiculite, and ferripyrophyllite $[\text{Fe}_3^+\text{Si}_4\text{O}_{10}(\text{OH})_2]$, nontronite, and other predominantly ferric iron clay minerals may not have formed at all. Furthermore, unaltered serpentines, smectites, and chlorites from stage 3 are likely to differ systematically in their transition metal chemistry from more recent samples in both major and minor elements. These distinctive characteristics of Hadean clays are potentially significant for origins-of-life scenarios, as smectites have long been invoked as catalysts for biosynthesis (Schoonen et al. 2004; Meunier et al. 2010), as templates for biomolecular assembly (Ferris and Ertem 1992; Ertem and Ferris 1997; Hanczyc et al. 2003; Chen et al. 2004; Deamer 2011), and even as possible self-replicating proto-life (Cairns-Smith 1968, 2005; Cairns-Smith and Hartman 1986).

Impact processes. An as yet little studied mechanism of clay mineral formation—one that played a significant mineralogical role only in the Hadean Eon—is hydrothermal activity associated with marginal zones of large impacts (Pirajno 2009; Hazen 2013). An estimated 20000 meteor impacts of objects >1 km diameter, with many impactors >10 km, altered Earth's near-surface mineralogy during the Hadean Eon (Glickson 1998). Each impact initially melted or vaporized surface phases within a radius significantly greater than that of the impactor, but such events also diversified Earth's mineralogy in three ways—the production of shock minerals, the excavation of high-pressure and temperature lithologies, and the generation of fracture zones with deep circumferential hydrothermal systems possibly lasting for >10⁵ years along crater margins (Abramov and Kring 2005; Versh et al. 2006; Pirajno 2009; Hazen 2013). A significant effect of impact hydrothermal alteration was thus production of clay minerals (Allen et al. 1982; Pirajno 2005).

Stage 4—Granitization (timing uncertain; >3.5 Ga)

The fourth stage of Earth's mineral evolution was characterized by extensive partial melting of basalt, the consequent production of extensive intrusive granitoid suites, and ultimately the formation of granitic protocontinents. While the exact timing of granite formation remains uncertain, we suggest that granite production by partial melting of basalt (stage 4) likely precedes plate tectonics (stage 5) on any terrestrial planet, and that granite formation is likely to occur on some planets that are too small to initiate plate tectonics. All of the aqueous alteration processes of mafic lithologies observed in stage 3 would have continued to operate throughout stage 4. Production of trioctahedral ferromagnesian clay minerals, for example via serpentinization and seawater-basalt interactions, would continue throughout Earth's history as major clay-forming mechanisms (albeit at a gradually decreasing rate, depending on exposure of basaltic crust to fluids and heat flow). However, as many as four modes of clay mineral paragenesis must have occurred significantly for the first time as a result of the emergence of granitic protocontinents: Al-silicate alteration, anoxic surface weathering, clay authigenesis, and formation of rare complex pegmatite clay minerals.

Al-silicate alteration. First, and most significantly for stage 4 clay paragenesis, aqueous and hydrothermal processes altered

extensive deposits of feldspars, feldspathoids, micas, and other Al-bearing minerals. Note that many of the common Al-bearing clay minerals probably occurred to a limited extent in stage 3 (Tables 1 and 2), but alteration of granite must have led to the first volumetrically significant production of several dioctahedral aluminous clay minerals, including kaolinite and its polymorphs (dickite, nacrite, and halloysite), aluminous smectites, vermiculite, and possibly pyrophyllite.

Numerous studies describe the aqueous and hydrothermal alteration of common rock-forming micas, most notably dioctahedral muscovite $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$ and the trioctahedral biotite group $[\text{K}(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})\text{Si}_3\text{O}_{10}(\text{F}, \text{OH})_2]$. Stoch and Sikora (1976), for example, described the alteration of biotite, muscovite, and secondary illite directly to kaolinite—a process reflected in the common occurrence of muscovite books containing interlayers of kaolinite. Indeed, many large deposits of kaolinite throughout the world contain remnant muscovite that served as the source for much of the kaolinite [e.g., the Georgia kaolin deposits: Jonas (1964)]. Where alteration was more gradual, micas may display the following characteristic reaction pathway (Weaver 1989)



In related studies, Meunier and Velde (1979) and Velde and Weir (1979) observed that altered granite hosts illite along grain boundaries between muscovite and alkali feldspar, and micas and K-feldspar (KAlSi_3O_8) also alter to vermiculite and beidellite. Kaolinite and Fe oxides can occur in fractured granites that experience relatively high water flow and, with time, granite may alter almost entirely to kaolinite and oxides, but it may also transform into other phases such as halloysite and gibbsite, depending on environmental conditions (Weaver 1989).

These studies thus indicate that a complex interplay of chemical and physical factors, including temperature, aqueous fluid composition (including activity ratios of cations to H^+), water/rock ratio, and fluid flow rates, is required to explain the varied modes of clay mineral paragenesis from alteration of Al silicate minerals. Temperature, in particular, plays an important role in the hydrothermal alteration of granite. Velde (1985) recognized four types of hydrothermal alteration of granite: potassic, phyllic, argillic, and propylitic, each of which results in different clay-bearing mineral assemblages that reflect different formation temperatures (Lowell and Guilbert 1970; McDowell and Elders 1980). Potassic alteration produces new K-feldspar and Mg-Al-bioite (i.e., with Mg and Al greater than in typical magmatic biotite: Moore and Czamanske 1973; Beane 1974; Jacobs and Parry 1976). Phyllic alteration produces sericite, whereas argillic alteration is notable for producing illite and mixed-layer clay minerals such as rectorite $[(\text{Na}, \text{Ca})\text{Al}_4(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$; a 1:1 ordered interstratification of illite and smectite] that may occur with kaolinite (Velde 1985). Finally, propylitic alteration is characterized by a pairing of chlorite and epidote $[\text{Ca}_2\text{Fe}^{3+}\text{Al}_2(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})]$ —an assemblage suggesting formation temperatures of ~200 °C (McDowell and Elders 1980).

Fluid pH also affects the observed clay mineral assemblage. Neutral to mildly acid conditions commonly result in allophane,

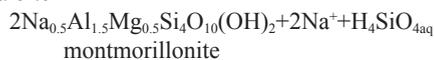
kaolinite, or halloysite, and kaolinite has been identified as a surface coating on weathered feldspars, often armoring the remaining feldspar crystal. As cation to H^+ activity ratios increase, which could correspond to pH increase, other minerals such as smectites form in the presence of cations such as K, Na, and Mg (Weaver 1989). Under strongly leached conditions, all species but Al are removed at moderate pH, resulting in precipitation of aluminum hydroxides, such as boehmite and diasporite [both $AlO(OH)$], and gibbsite, and ultimately the formation of bauxite (Wollast 1967; Weaver 1989). It should be noted that the existence of Paleoproterozoic or Mesoproterozoic bauxite deposits is by no means certain. If extensive granitic protocontinents formed by ~ 3.5 Ga, then development of such Al-rich clay horizons and bauxite is plausible. However, paleobauxites older than the Paleoproterozoic Era are rare (Adusumalli and Schubert 2001).

Finally, the flow rate of the aqueous fluid (or water-to-rock ratio) strongly influences feldspar alteration and clay mineral formation: At low or stagnant flow rates, for example, montmorillonite (or illite) forms, whereas kaolinite and gibbsite form at successively higher flow rates, reflecting progressively increased Al/Si in the mineral phase (Berner 1971; Weaver 1989).

Stagnant or very low-flow rate



albite



montmorillonite

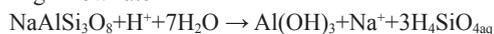
Moderate flow rate



albite

kaolinite

High-flow rate



albite

gibbsite

Thus, high flow-rates and/or water-rock ratios favor more aluminous mineral assemblages.

Anoxic-surface weathering. Surface weathering in the absence of molecular oxygen, which represents a second new mode of clay mineral paragenesis associated with growing granitic continents, increased opportunities for soil formation with both di- and trioctahedral Mg-Fe-Al clay minerals, including possibly illite, sepiolite, vermiculite, and kaolinite. Of special importance was subaerial or near-surface alteration of silicic volcanic tuff, which may have led to extensive deposits of montmorillonite-rich bentonites (Caballero et al. 1985; Linares 1985, 1987; Christidis and Huff 2009). Montmorillonite, beidelite, and nontronite, the most common dioctahedral smectites, are also found in hydrothermally altered volcanic and igneous rocks (Bischoff 1972; Murnane and Clague 1983; Thompson et al. 1985; Singer and Stoffers 1987; Alt 1988; Hekinian et al. 1993). Montmorillonite and related smectites have been invoked in several prominent theories of life's origins (e.g., Cairns-Smith and Hartman 1986; Ferris and Ertem 1992; Ertem and Ferris 1997; Meunier et al. 2010), although other clay mineral species may be equally well suited for prebiotic chemistry. Clay mineral diversification is significant, therefore, because a planet may

have to progress through at least this stage of mineral evolution as a prerequisite for life.

Clay authigenesis. A third mechanism of clay mineral formation that likely arose in stage 4 is authigenesis of dioctahedral clays. The erosion of granitic continents led to the first significant marine Al-rich sedimentary deposits, where detrital clay minerals from the subaerial crust would have augmented authigenic clay mineral formation. Illite, illite/smectite, berthierine, Al-bearing chlorite, and dickite are all possible authigenic clays from stage 4. In addition, we suggest that the rare aluminous phyllosilicate clay mineral donbassite [$Al_2(Si_3Al)O_{10}(OH)_2 \cdot Al_{2.33}(OH)_6$], which forms by authigenesis in Al-rich sediments, may have appeared for the first time in stage 4.

Complex pegmatite clay minerals. Yet another consequence of granitization, albeit a gradual one that may have taken a billion years of fluid-rock interaction, was the formation of complex pegmatites and their associated suites of the minerals of Li, Be, B, and other incompatible elements (London 2008; Grew and Hazen 2009, 2010a, 2013; Bradley 2011; Tkachev 2011). Complex pegmatites are known to host five unusual clay minerals that arise from hydrothermal alteration of primary pegmatite minerals, all of which probably appeared for the first time in stage 4 (Tables 1 and 2). For example, swinefordite [$Ca_{0.2}(Li,Al,Mg,Fe)_3(Si,Al)_4O_{10}(OH,F)_2 \cdot nH_2O$] is a dioctahedral Li-rich smectite that forms by alteration of the lithium clinopyroxene spodumene ($LiAlSi_2O_6$). Similarly, the serpentine-group mineral manandonite [$Li_2Al_4(Si_2AlB)O_{10}(OH)_8$], and the chlorite-group minerals cookeite [$(Al,Li)_3Al_2(Si,Al)_4O_{10}(OH)_8$] and borocookeite [$LiAl_4(Si_3B)O_{10}(OH)_8$], are rare clay minerals that form from alteration of tourmaline-group minerals and/or Li-bearing mica ("lepidolite"). In addition, yofortierite [$Mn_3^2+Si_8O_{20}(OH)_2 \cdot 8-9H_2O$] is found exclusively in sodalite-nepheline syenite pegmatites enriched in Mn. Other clay minerals formed from weathering of complex pegmatites, although not new species, may display unusual minor-element compositions. The rare Cs-bearing muscovite "namingite," for example, weathers to a Cs-bearing illite or smectite. Such Cs-rich clay minerals are very rare in nature but are easily produced by cation-exchange experiments in the laboratory.

Stage 5—Plate tectonics (timing uncertain; >3.0 Ga)

Stage 5 marked the beginning of plate tectonics on Earth—a time that initiated sediment recycling into the mantle at subduction zones (e.g., Koster van Groos 1988) and significantly increased the scale of fluid-rock interactions in the overlying upper mantle and crust. Unfortunately, the minimal rock record prior to 3.5 Ga obscures the chronology of early subduction, orogenic processes, the formation of the cratons, and the assembly of the first continents. The transition from plume-dominated to modern-style plate tectonics for the first time resulted in the orderly accretion of granitic terrains into continents. However, major unresolved questions relate to the timing and rate of continent formation. Estimates range from essentially modern continental coverage by the end of the Hadean Eon at ~ 4 Ga, to continued continental growth into the late Archean Eon at <3 Ga (Condie 1989; Rogers and Santosh 2004; Harrison et al. 2005; Smithies et al. 2005a, 2005b; Stern 2005; Witze 2006; Dewey 2007; Groves and Bierlein 2007; Rollinson 2007; Condie and Pease 2008;

Van Kranendonk 2011; Cawood et al. 2013; Nance et al. 2013). Similar uncertainties apply to the nature and extent of soils in the Archean Eon. While most land surface prior to the evolution of the terrestrial biosphere was subject to denudation by rainfall and runoff, at what point in Earth history would significant mud deposits have accumulated in terrestrial depressions?

All of the previously mentioned modes of clay mineral paragenesis operated throughout the initiation of plate tectonics. Aqueous and hydrothermal alteration of a wide range of ultramafic to acidic lithologies produced abundant trioctahedral (Mg-Fe²⁺) and dioctahedral (Al) clays in the shallow oceanic and continental crust. Growing marine sediment deposits were the loci of authigenic clay formation, whereas anoxic protocontinent weathering may have produced clay-rich terrestrial sedimentary deposits in lakes and valleys.

Plate tectonics also resulted in orogenic processes associated with convergent margins, which exposed significant expanses of deep metamorphic lithologies for the first time. Greenschist facies metamorphic rocks rich in clinocllore, chamosite, and other chlorite-group minerals thus were added to the near-surface environment. In particular, metamorphic Mn- and Ni-chlorites, pennantite [(Mn²⁺,Al)₆(Si,Al)₄O₁₀(OH)₈] and nimitite [(Ni,Mg,Al)₆(Si,Al)₄O₁₀(OH)₈], appeared during stage 5 as a result of the metamorphism and subsequent uplift of Mn and Ni deposits. Thus, whatever the timing, tectonic activity and its associated alteration of near-surface mineralogy, metamorphism, and an increased volume of the crust affected by hydrothermal activity could have increased the number of mineral phases to ~1500, including 37 of the 56 phyllosilicate clay mineral species listed in Tables 1 and 2, prior to the biological innovations of stage 6.

Stage 6—The anoxic microbial world (3.9–2.4 Ga)

Biological processes began to affect Earth's surface mineralogy by the Eoarchean (~3.9 to 3.6 Ga), when large-scale surface mineral deposits were precipitated under the influences of changing atmospheric and ocean chemistry (e.g., Hazen et al. 2008, 2009). There is no evidence for a significant terrestrial biota at this time, nor were marine microbial populations sufficiently diverse or widespread to have had a major impact on clay mineral formation.

It is likely that all modes of clay mineral paragenesis observed in stages 2 through 5 (i.e., aqueous and hydrothermal alteration, authigenic formation in sediments, anoxic surface weathering, and low- to moderate-grade metamorphic formations exposed by tectonic processes) were active throughout stage 6. One possible mineralogical novelty associated with early life may have been the local production of clay minerals with increased Fe³⁺/Fe²⁺, perhaps in zones associated with biologically mediated ferrihydrite [Fe₄₋₅(OH, O)₁₂] and banded iron formations (Konhauser et al. 2005; Kendall et al. 2012). Thus, greenalite and minnesotaite [(Fe²⁺)₃Si₄O₁₀(OH)₂] may have occurred for the first time. However, it is also likely that anoxic zones hosted populations of iron-reducing microbes, which are known to alter dioctahedral smectite, illite, and chlorite (Dong et al. 2009).

In addition, clay minerals that form through alteration of carbonate-rich zones, including skarn minerals, may also have increased significantly as a consequence of bio-

logically precipitated carbonate platforms. Thus, stage 6 may have seen enhanced production of antigorite and kellyite [(Mn²⁺,Mg,Al)₃(Si,Al)₂O₅(OH)₄] (Table 2).

Stage 7—The great oxidation event (2.4–2.2 Ga)

The Paleoproterozoic “Great Oxidation Event” (GOE), when atmospheric oxygen may have risen to >1% of modern levels, initiated a remarkable, if prolonged, diversification of Earth's near-surface mineralogy as a consequence of oxidative weathering. Hazen et al. (2008, 2009) estimated that more than 2500 new minerals appeared for the first time after the stabilization of high-oxidation states of Fe, Ni, Mn, Cu, Hg, Mo, U, and other redox-sensitive elements. Biochemical processes may thus be responsible, directly or indirectly, for the majority of Earth's >4800 known mineral species.

Stage 7 of Earth's mineral evolution likely saw the first appearance, or at least the first volumetrically significant formation, of at least 13 phyllosilicate clay minerals (Tables 1 and 2). Most of these new phases are ferric iron clay minerals, such as the halloysite isomorph hisingerite, which forms by oxidative weathering of Fe silicates (including Fe-smectites) or sulfides (Kohyama and Sudo 1975); the serpentine group-minerals cronstedtite [(Fe³⁺Fe²⁺)₃(Si,Fe³⁺)₂O₅(OH)₄] and odinite [(Fe³⁺,Mg,Al,Fe²⁺)_{2.5}(Si,Al)₂O₅(OH)₄]; the sepiolite/palygorskite-group mineral tuperssuatsiaite [NaFe³⁺Si₈O₂₀(OH)₂·4H₂O]; the smectite-group mineral nontronite; the Fe³⁺ isomorph of pyrophyllite, ferripyrophyllite, which forms both by hydrothermal alteration in oxic environments and by precipitation from hot and highly saline solutions (Badaut et al. 1992); and glauconite. Glauconite forms in marine sediments, commonly on continental shelves in proximity to organic matter, which provides a reductive local environment. Glauconite formation is often microbially mediated and is controlled by diffusion of K from seawater and Fe²⁺ from iron minerals (Odin 1988; Meunier and El Albani 2007). Glauconite may also form from biotite by marine diagenesis in shallow water under reducing conditions.

Several clay minerals are known only from the oxidized weathering zones of ore bodies and thus also likely postdate the Great Oxidation Event. Examples include the serpentine-group minerals brindleyite [(Ni,Al)₃(Si,Al)₂O₅(OH)₄] and fraipontite [(Zn,Al)₃(Si,Al)₂O₅(OH)₄]; the smectite-group minerals sauconite [Na_{0.3}Zn₃(Si,Al)₄O₁₀(OH)₂·4H₂O], zincsilitite [Zn₃(Si,Al)₄O₁₀(OH)₂·4H₂O], and yakhontovite [(Ca,Na,K)_{0.2}(Cu,Fe,Mg)₂Si₄O₁₀(OH)₂·3H₂O]; and the chlorite-group minerals gonyerite [Mn²⁺Fe³⁺(Si₃Fe³⁺)O₁₀(OH)₈] and baileychlorite [(Zn,Fe²⁺,Al,Mg)₆(Si,Al)₄O₁₀(OH)₈].

The GOE also must have resulted in expanded compositional ranges of numerous other clay minerals as Fe³⁺ increasingly occupied both octahedral and tetrahedral sites, with a corresponding shift to additional dioctahedral clay mineral phases. For example, ferric iron-rich varieties of vermiculite would have arisen during the oxidative weathering of stage 7 (Velde 1985). Although the GOE would not have immediately triggered dramatic increases in the production of Fe³⁺ minerals in anoxic deep ocean environments, it would have begun a significant modification in the aqueous chemistry of Fe, because iron became less soluble as waters became oxygenated: marine Fe²⁺ would have gradually been depleted by precipitation of Fe-oxyhydroxides (Anbar and Knoll 2002; Klein 2005).

Stage 8—The intermediate ocean (2.0–1.0 Ga)

The billion years following the Great Oxidation Event encompass one of the most enigmatic stages of Earth's mineral evolution. We suggest that few new species of clays arose, as no significant changes in environmental conditions occurred. All pre-existing modes of clay mineral paragenesis continued, and ongoing sedimentation and recycling via plate tectonics gave rise to increasing volumes of phyllosilicate-bearing rocks. It is worth noting that many clay minerals were being recycled by this point in Earth history, through subduction, regional metamorphism, charnockitization (e.g., Janardhanan et al. 1979; Newton et al. 1980), and other processes. Thus, clay minerals were both added and removed from the near-surface environment (i.e., Koster van Groos 1988).

A caveat to the model of the intermediate ocean as a time of stasis relates to the assembly of the Columbian and Rodinian supercontinents at ~2.0–1.8 and ~1.2–1.0 Ga, respectively. Several studies have demonstrated pulses of mineralization and associated mineral diversification during those intervals (Meyer 1981; Grew and Hazen 2009, 2010a, 2013; Condie and Aster 2010; Bradley 2011; Condie et al. 2011; Tkachev 2011; Hazen et al. 2012; Golden et al. 2013). If hydrothermal activity associated with collisional orogenies led to mineralization, then clay mineral formation must have been enhanced during those intervals as well. Furthermore, rifting of Columbia at ~1.6–1.2 Ga (e.g., Nance et al. 2013) was accompanied by deposition of thick marginal sediment wedges, which also provided loci for clay formation and accumulation.

Stage 9—The Snowball Earth (1.0–0.542 Ga)

Dramatic changes in the production of clays and many other minerals occurred during the Neoproterozoic Era, which saw extreme fluctuations in the near-surface environment, coupled with significant biological innovations. These changes include alternating snowball and hothouse climate episodes, increases in atmospheric oxygen, the breakup of the Rodinian supercontinent, and the rise of multicellular animals.

At least two major glaciation events between 750 and 650 Ma interrupted the terrestrial weathering cycle, as near-surface reaction rates slowed greatly due to decreased temperatures, limited availability of liquid water, and the effects of an extensive ice veneer that may have extended from poles to the Equator. We suggest that only subsurface aqueous/hydrothermal alteration and highly localized oxic weathering of volcanic edifices produced significant clay minerals during Snowball Earth episodes, although authigenic clay mineral formation would have continued in the oceans. Minor production of clay minerals may also have occurred via low-temperature alteration of rock flour beneath abundant glaciers.

Clay mineral formation must have been correspondingly elevated during intervals between Snowball Earth episodes, characterized by relatively brief (~10 Ma) "hothouse" periods of rapid warming triggered by elevated CO₂ concentrations and greenhouse gas warming, reinforced by positive albedo feedbacks as ice caps retreated. Increased surface weathering and nutrient-rich runoff, coupled with high-atmospheric CO₂, led to extensive algal blooms and significant increases in atmospheric O₂, as well.

Perhaps the most significant impact of oxygenation is that it ultimately gave rise to today's range of biochemical mechanisms. Microbial activity enhances clay mineral production, for example by the bio-weathering of feldspar and mica (Schwartzman and Volk 1989; Paris et al. 1995; Bennett et al. 1996; Barker et al. 1998; Ueshima and Tazaki 1998, 2001; Ueshima et al. 2000; Tazaki 2005), as well as via microbially mediated oxidation and reduction reactions (Shelobolina et al. 2003; Kim et al. 2004; Fisk et al. 2006; Stucki and Kostka 2006; Dong et al. 2009; Bishop et al. 2011; Dong 2012). A terrestrial photosynthetic biota may have arisen as early as ~850 Ma (Knauth and Kennedy 2009; Hand 2009), and a significant Neoproterozoic increase in clay mineral deposition may have been the result of microbial activity in soils. These processes possibly led to the so-called "clay mineral factory" (Kennedy et al. 2006). Alternatively, Tosca et al. (2010) suggest that the Neoproterozoic Era saw a relative shift in chemical vs. physical weathering, with no significant increase in total clay mineral production.

An indirect consequence of increased microbial activity was the enhanced marine sequestration of organic carbon within clay floccules and onto clay mineral surfaces (Hedges and Keil 1995; Mayer et al. 2004). Clay mineral surfaces actively adsorb several organic compounds, particularly polar organic molecules, and clay minerals can participate in reactions that modify the organic molecules (Ransom et al. 1997, 1998, 1999; Blair and Aller 2012). In addition, it has often been inferred that clay minerals can play a role in protecting organic molecules from subsequent oxidation and other reactions, thereby effectively preserving the organic molecules (Gordon and Millero 1985; Baldock and Skjemstad 2000; Lalonde et al. 2012). Subsequent burial of this organic carbon with clay minerals, which was possibly the first major global-scale carbon sequestration process, contributed to a rise in atmospheric oxygen by decreasing the opportunity for organic carbon to oxidize.

Stage 10—Phanerozoic biomineralization (0.542 Ga to present)

The Neoproterozoic rise in atmospheric oxygen, with the consequent formation of the UV-blocking ozone layer, ultimately facilitated the evolution of multicellular life and led to skeletal biomineralization—events that irreversibly transformed Earth's near-surface mineralogy. Skeletal biomineralization of carbonates had the indirect effect of sequestering large amounts of carbon in Earth's crust, further modifying the composition of the atmosphere, and changing the pH of the oceans. The rise in oxygen also altered Earth's surficial aqueous geochemistry, changing near-surface redox chemistry (most importantly for Fe in the context of clay minerals) as well as minor and trace element speciation.

Soil formation. Grim (1968), Velde (1985), Newman (1987), and Weaver (1989) provide overviews of rock weathering, soil formation, and phyllosilicate clay mineralogy resulting from near-surface rock alteration. Weathered rocks are not altered homogeneously; rather they develop rock alteration horizons, grading from the deepest unaltered rock, through saprock, saprolite, laterite, and the topmost soil layer. Resulting clay mineral assemblages can therefore be classified into chemical systems based on their alteration processes and conditions. For

example, alkali, alkaline earth, and Fe^{2+} minerals tend to decrease upward, whereas Al, Fe^{3+} , and hydrated species increase toward the soil horizon (Velde 1985; Newman 1987; Weaver 1989). These details, particularly with respect to redox-sensitive elements such as Fe, would differ significantly on Earth before the Great Oxidation Event or before biological activity was important on the surface.

Details of weathering profiles also differ significantly depending on the primary lithology. The two most important factors controlling the weathering of komatiites and other ultramafic rocks are the loss of Mg from the rocks and oxidation of Fe. Prior to about 2.4 Ga (the start of the Great Oxidation Event), ultramafic rocks probably did not experience significant oxidation (Sverjensky and Lee 2010). However, after 2.4 Ga, oxidation became much more important to the evolution of Earth's clay minerals, primarily by oxidation of Fe^{2+} to Fe^{3+} (a process that was accelerated by microbially mediated redox reactions; e.g., Cheah et al. 2003; Shelobolina et al. 2003; Bishop et al. 2011).

Loss of Mg in ultrabasic rocks does not contribute substantially to soil clay minerals because Mg-saponite, chlorite, sepiolite, or palygorskite are unstable during weathering (Velde 1985). In this regard the role of Mg in solution is of special interest. Harder (1972) investigated smectite paragenesis at surface conditions and concluded that the presence of Mg in solution favors the formation of smectite minerals. He found that montmorillonite and talc can be synthesized from Mg-hydroxide silica gel, but Mg-Al-hydroxide silica gel precipitated both di- and trioctahedral smectites. Low silica was observed to be favorable for formation of montmorillonite, a significant result given the predominantly ultramafic to mafic crustal composition of early Earth, and a result at odds with recent research supporting the formation of smectites under high-silica activity conditions (Bish and Aronson 1993; Abercrombie et al. 1994).

Olivine weathering would have provided the needed chemical reactants for such reactions, so saponite is likely to have been a significant clay mineral from the earliest stages of Earth history. Indeed, Mg-rich clay minerals such as saponite appear to be a common alteration product of the ancient basaltic crust of Mars (e.g., Poulet et al. 2005; Bibring et al. 2006; Mustard et al. 2008; Ehlmann et al. 2009, 2010; Milliken et al. 2009; Carter et al. 2010; Milliken and Bish 2010).

Oxidative weathering of mafic lithologies yields a distinctive sequence of clay minerals. For example, Ildefonse (1980) described weathering of a metagabbro with a saprock zone of Fe beidellite, nontronite, and talc, as well as Fe oxides overlying a saprolite zone containing coarse-grained vermiculite. This sequence reflects a loss of Ca and Mg coupled with Fe oxidation. Note that iron oxidation facilitates the transition from tri- to dioctahedral clay minerals [$(\text{Fe}^{2+})_3 \rightarrow (\text{Fe}^{3+})_2$]; i.e., serpentine, chlorite, and/or saponite transform to nontronite as follows (Ducloux et al. 1976): chlorite + trioctahedral smectite \rightarrow dioctahedral smectite + interstratified minerals.

Alteration of ultramafic rocks under humid conditions commonly results in formation of laterites that contain various phyllosilicates, including vermiculite, chlorite, kerolite, and smectites (including Ni-bearing varieties). Vermiculite (di- or trioctahedral) is commonly produced during basic rock weathering (Jackson et al. 1952; Bassett 1959; Rich and Cook 1963; Johnson 1964;

Tardy and Gac 1968; Proust 1982; Velde 1985). Vermiculite paragenesis often reflects a coupled loss of K, Ca, and Mg, together with oxidation of Fe. Crystallization occurs in response to the incorporation of more Al and Fe^{3+} in the octahedral sites from the leaching of Mg and oxidation of Fe^{2+} (Velde 1985).

Weathering of granite and other felsic rocks contrasts with the alteration of more mafic lithologies. Kaolinite is present with oxides in the fracture systems of granites but has a minor effect on the mass balance of the system (Meunier 1980; Newman 1987). Gibbsite is common in the lowest parts of granitic alteration profiles and the rock may also be kaolinized (Helgeson 1970; Calvert et al. 1980; Macias-Vazquez 1981; Newman 1987). Feldspar weathering in acidic lithologies is influenced by several factors. Composition strongly affects feldspar dissolution rates, and Na and Ca removal rates are greater than for K. Thus, plagioclase weathers more rapidly than K-feldspar and mica (Johnson et al. 1968; Nesbitt et al. 1980; Nesbitt and Young 1984; Weaver 1989).

The role of root systems. Fungi and plants, which established a terrestrial foothold ~430 Ma, dramatically changed the rate of terrestrial mineral alteration to clays. Plant root systems change soil chemistry by producing organic acids that accelerate clay mineral formation (Weed et al. 1969; Silverman and Munoz 1970; Huang and Keller 1970, 1972; Kodama et al. 1983). For example, fulvic acid has been used to facilitate synthesis of kaolinite at low temperatures (Siffert 1978). It is likely, therefore, that organic acids began to play an important role in many low-temperature, near-surface mineral dissolution reactions soon after the development of surface vegetation.

Plant roots also facilitate removal of potassium from biotite (Spyridakis et al. 1967; Cecconi et al. 1975; Weaver 1989); thus micas serve as a biological source of potassium as they alter to vermiculite (Bassett 1959) and eventually to kaolinite. A major effect of plants on clay mineral chemistry was the differential removal of cations other than Si, thereby gradually transforming soil horizons to more silicious minerals, including smectites, illites, and kaolinite, compared with oxide-hydroxides such as gibbsite (B. Velde, personal communication). Plants also dramatically increased the volume of terrestrial clay minerals: Throughout the Paleozoic Era, plants established progressively deeper soil profiles, which provided the foundation for progressively taller plants. Thus, terrestrial clay mineral formation exemplifies the co-evolution of the geo- and biospheres.

Few of the 56 IMA recognized phyllosilicate clay mineral species appeared in the Phanerozoic Eon for the first time. The serpentine-group mineral odinite [$(\text{Fe}^{3+}, \text{Mg}, \text{Al}, \text{Fe}^{2+})_{2.5} (\text{Si}, \text{Al})_2 \text{O}_5 (\text{OH})_4$] is known today only as an authigenic species in tropical reefs. The sepiolite-group mineral loughlinitite [$\text{Na}_2 \text{Mg}_3 \text{Si}_6 \text{O}_{16} \cdot 8 \text{H}_2 \text{O}$], a product of dolomite alteration, and the soil mineral palygorskite are found exclusively in Phanerozoic formations and may thus also be restricted to stage 10. Similarly, if laterite formation is a unique characteristic of the terrestrial biosphere then the rare species orthochamosite [$\text{Fe}_5^{2+} \text{Al} (\text{Si}, \text{Al}) \text{O}_{10} (\text{O}, \text{OH})_8$] and falcondoite [$\text{Ni}_4 \text{Si}_6 \text{O}_{15} (\text{OH})_2 \cdot 6 \text{H}_2 \text{O}$] are also found only in stage 10. Given the varied clay-forming environments of the Phanerozoic Eon, we speculate that all 56 clay species cited in Table 2 have formed during the past 500 Ma (and likely still are forming).

PHANEROZOIC CLAY MINERALS AND ATMOSPHERIC CHEMISTRY

Studies of clay mineral evolution are hindered by early Earth's meager clay mineral record—the consequence of burial, alteration, subduction, and erosion. Accordingly, much of the preceding analysis has relied on speculation based on studies of clay mineral stabilities and mechanisms of contemporary clay mineral paragenesis. However, detailed compilations of the temporal distribution of clay minerals over the past 1.3 Ga, and especially the last 600 Ma, by Ronov and coworkers provide an unparalleled record of relative clay abundances during the late Proterozoic and Phanerozoic Eons and thus offer the possibility of a more quantitative statistical approach to clay mineral evolution. Especially useful in this regard is the geographically extensive and sample intensive compilation of Ronov et al. (1990) for select clay-group mineral abundances from ~10,000 dated shale samples to 1300 Ma from the Russian platform. Ronov and colleagues analyzed the modal abundances of four predominant groups of clay minerals, as distinguished by their characteristic (001) X-ray diffraction peaks—kaolinite group (7 Å), illite group (10 Å), “montmorillonite” (i.e., smectite group; expandable ≥ 10 Å), and chlorite group (14 Å)—for each shale sample.

Starting with the assumption that terrestrial clay mineral abundances may reflect both diagenetic processes and variations in atmospheric composition, we examined correlations between pairs of clay mineral abundances vs. time, as well as for clay abundances vs. recent quantitative models of global O_2 and CO_2 levels in Earth's atmosphere extending back 543 Ma through the Phanerozoic Eon (Berner 2004, 2006a, 2009; Arvidson et al. 2007).

We find two significant pair correlations between the relative abundances of clay mineral groups. As expected, the most significant correlation is found for sediment concentrations of the two most abundant clay mineral groups, illite and smectite [“montmorillonite” of Ronov et al. (1990)]. Illite-group clay minerals dominate in sediments of the early Phanerozoic Era but

¹ Deposit item AM-13-1106, Supplemental Tables 1–4 and text. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

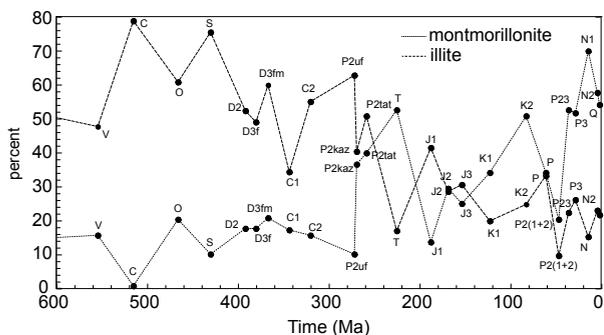


FIGURE 1. Relative abundances of smectite- vs. illite-group clay minerals during the Phanerozoic Eon. Data for Russian platform sediments from Ronov et al. (1990). Labels represent abbreviations for geologic time intervals (Supplementary Table 1').

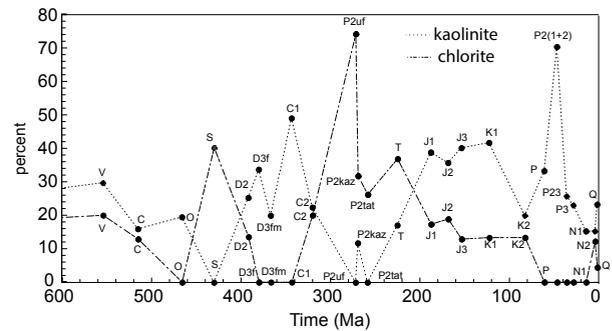


FIGURE 2. Relative abundances of chlorite- vs. kaolinite-group clay minerals during the Phanerozoic Eon. Data for Russian platform sediments from Ronov et al. (1990). Labels represent abbreviations for geologic time intervals (Supplementary Table 1').

tend to be less abundant in more recent formations. Smectite-group minerals, on the other hand, are more abundant in younger sediments (Fig. 1). We employed the Pearson product-moment correlation coefficient (PMCC; see Supplementary Text¹) to quantify the negative correlation of illite with smectite (PMCC = -0.74)—a significant overall trend that is consistent with the well-known alteration sequence from smectite to illite during burial diagenesis (Hower et al. 1976; Weaver 1989).

We also observe a significant negative correlation (PMCC = -0.55) between kaolinite and chlorite, which are the least abundant of the four clay mineral groups reported in these samples (Fig. 2). This result suggests that a significant amount of kaolinite might be derived from weathering of chlorite, probably during the weathering of mafic volcanic rocks—a major process in the GEOCARBSULF model (Berner 2006b; see below).

In addition to the diagenetic smectite-illite and chlorite-kaolinite transitions, we find four significant correlations between clay mineral abundances and atmospheric chemistry—correlations that may reflect net effects of geological processes such as weathering, sedimentation, metamorphism, and hydrothermal alteration, as well as biological processes such as photosynthesis, bacterial sulfate reduction, and Fe^{2+} oxidation. Variations in the relative abundances of the clay mineral groups kaolinite, illite, smectite, and chlorite in shales on a regional spatial scale have been correlated with changes in climate, particularly humidity, during parts of the Paleozoic Era (Ronov et al. 1990; Hallam et al. 1991; Hesselbo et al. 2009), and it has been hypothesized that Neoproterozoic clay mineral production increased globally in association with a rise in O_2 level (Kennedy et al. 2006; but see also Tosca et al. 2010). However, correlations between atmospheric composition and relative clay mineral group abundances have not been reported.

The procedure used in Ronov et al. (1990) provides a platform-wide average over different clay mineral depositional environments and assumes a uniform and similar diagenetic history for all samples—an assumption that is at best an approximation. We suggest that by correlating relative abundances of different clay mineral groups with atmospheric CO_2 and O_2 , we test the extent to which variations in relative proportions of clay mineral groups reflect their genesis in a weathering

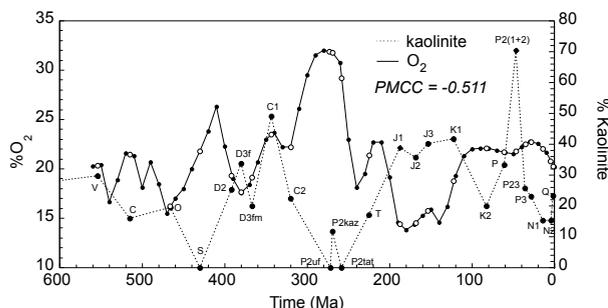


FIGURE 3. Relative abundance of kaolinite-group minerals in shales from the Russian platform (Ronov et al. 1990) vs. values of the level of atmospheric O_2 from the GEOCARBSULF model (Berner 2006a) as functions of age. Labels represent abbreviations for geologic time intervals (Supplementary Table 1¹). Closed circles on O_2 curve are model calculations; open circles are interpolations to times of sampled clays. PMCC = Pearson moment correlation coefficient (see text).

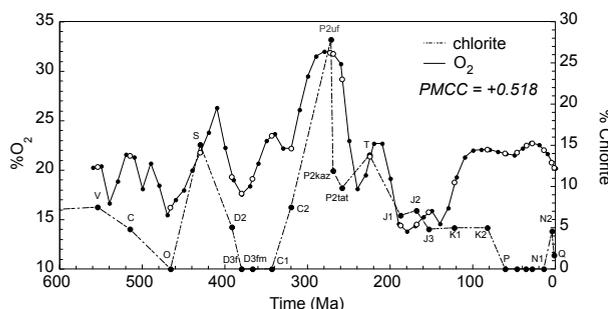


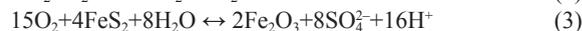
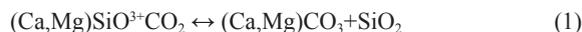
FIGURE 4. Relative abundance of chlorite-group minerals in shales from the Russian platform (Ronov et al. 1990) vs. values of the level of atmospheric O_2 from the GEOCARBSULF model (Berner 2006a) as functions of age. Labels represent abbreviations for geologic time intervals (Supplementary Table 1¹). Closed circles on O_2 curve are model calculations; open circles are interpolations to times of sampled clays. PMCC = Pearson moment correlation coefficient (see text).

environment, as opposed to diagenetic and other factors. For example, illite commonly forms by diagenetic alteration of K-feldspars, as well as by the progressive transformation of smectite evident in Figure 1. We assumed that each sample is representative of a global environmental condition for a specific geologic age (Gradstein et al. 2004). We plotted relative abundances of the four clay mineral groups (Supplementary Tables 1 and 2¹) as time series with the model-calculated O_2 or CO_2 levels from GEOCARBSULF (Berner 2006a, 2009; Figs. 3–6; Supplementary Table 3¹), which employs a chronology consistent with Gradstein et al. (2004). Similar correlations were obtained using the CO_2 model values from the Magic model (Arvidson et al. 2007), but O_2 values for the entire Phanerozoic Eon were not reported by these authors and may differ from those in GEOCARBSULF.

A matrix of eight possible correlations between the four different clay mineral groups and O_2 and CO_2 levels is given in Supplementary Table 4¹. We find four significant correlations (i.e., PMCC < -0.5 or PMCC > 0.5) between the Ronov et al. (1990) clay abundance data and the Berner (2009) atmospheric composition model for CO_2 and O_2 , as described below.

Kaolinite and chlorite vs. O_2

Figure 3 illustrates a negative correlation between the relative abundance of kaolinite and O_2 levels over the entire Phanerozoic Eon (PMCC = -0.51), in contrast to the lack of significant correlation with CO_2 levels (PMCC = -0.14). The O_2 and CO_2 levels in the GEOCARBSULF model (Berner 2006a) are controlled by the following overall reactions:



Equation 1 exerts primary control on CO_2 levels, whereas O_2 levels are controlled primarily by Equation 2 and are also influenced by Equation 3. Low levels of O_2 in Figure 3 correspond to net model shifts of Equation 2 to the left and Equation 3 to the right; both shifts are associated with higher levels of acidity.

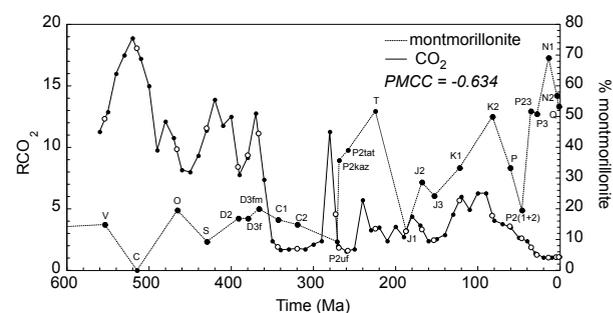


FIGURE 5. Relative abundances of smectite-group minerals (reported as “montmorillonite”) in shales from the Russian platform (Ronov et al. 1990) vs. values of the level of atmospheric CO_2 from the GEOCARBSULF model (Berner 2006a) as functions of age. RCO_2 denotes CO_2 concentration relative to present-day. Labels represent abbreviations for geologic time intervals (Supplementary Table 1¹). Closed circles on CO_2 curve are model calculations; open circles are interpolations to times of sampled clays. PMCC = Pearson moment correlation coefficient (see text).

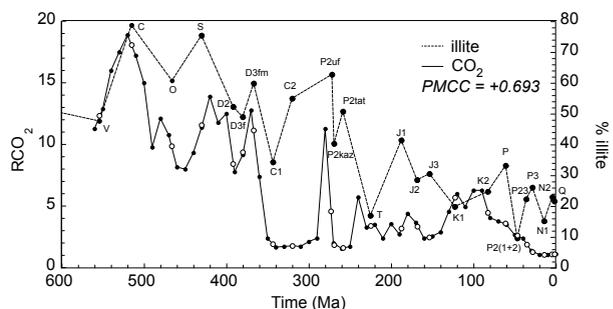


FIGURE 6. Relative abundances of illite-group minerals in shales from the Russian platform (Ronov et al. 1990) vs. values of the level of atmospheric CO_2 from the GEOCARBSULF model (Berner 2006a) as functions of age. RCO_2 denotes CO_2 concentration relative to present-day. Labels represent abbreviations for geologic time intervals (Supplementary Table 1¹). Closed circles on CO_2 curve are model calculations; open circles are interpolations to times of sampled clays. PMCC = Pearson moment correlation coefficient (see text).

If we assume that kaolinite is detrital and originally derived by weathering of silicates, then higher acidity during weathering corresponds to lower values of the ratios of aqueous cations to H^+ , e.g., $(a_{Mg^{2+}})/(a_{H^+})^2$ or $(a_{Ca^{2+}})/(a_{H^+})^2$, which favor the kaolinite stability field relative to Ca- and/or Mg-bearing silicates on aqueous activity diagrams (Drever 1988). Low- O_2 levels thus correspond to greater amounts of kaolinite relative to primary silicates or other clay minerals. It should also be emphasized that it is the weathering of Ca- and/or Mg-bearing silicates that is of the greatest global importance for the coupled O_2 and CO_2 cycles, because it is Ca and Mg that form carbonates in the oceans (Berner 2006a).

Relative abundances of chlorite through time (Fig. 4) correlate positively with O_2 levels over the Phanerozoic Eon as a whole (PMCC = +0.52), whereas no correlation occurs with CO_2 levels (PMCC = -0.04). These results suggest that chlorite could have formed by direct oxidative weathering of other mafic silicates at values of $(a_{Mg^{2+}})/(a_{H^+})^2$ unfavorable for kaolinite. However, some of the observed chlorite-group minerals could represent detrital phases, whose relative abundance is a monitor of what could be termed chemically assisted physical weathering, particularly of mafic and ultramafic rocks that contain chlorite from prior hydrothermal alteration processes. It is likely that physical weathering of such rocks rich in Mg^{2+} and Fe^{2+} (and also containing Fe^{3+}) was assisted by high levels of O_2 , which would oxidize any rapidly weathering Fe^{2+} -bearing minerals (e.g., olivine) to iron oxides and facilitate mechanical breakup of the rocks, resulting in a greater relative abundance of residual, ultimately detrital, chlorite.

Figure 4 suggests that the above modes of weathering were important from 550 Ma until about 200 Ma ago, after which the correlation between chlorite and O_2 appears weak. Interestingly, ~200 Ma ago corresponds to the rise of ectomycorrhizal fungi (EMF; Taylor et al. 2009). EMF are distinguished from the earlier arbuscular mycorrhizal fungi (AMF) by their ability to secrete oxalate and siderophores, which in combination have been shown in laboratory experiments to be particularly effective in solubilizing Fe-oxide (Cheah et al. 2003). EMF can facilitate solubilization of Fe-bearing minerals (Courty et al. 2010) and mechanical-chemical weathering of sheet silicates (Bonneville et al. 2009), which, in turn, could facilitate the incorporation of Fe^{2+}/Fe^{3+} into weathering products such as smectites. Thus the rise of EMF at about 200 Ma would have resulted in a complex style of combined physical, chemical, and biological weathering similar to that at the present day. We suggest that this new weathering behavior is reflected in the relative abundance of both chlorite- and smectite-group (see below) minerals from about 200 Ma to the present.

Smectite and illite vs. CO_2

Relative abundances of smectite-group minerals vs. time correlate with decreasing CO_2 levels (Fig. 5; PMCC = -0.63). Unlike kaolinite- and chlorite-group minerals, smectite abundance is not correlated with O_2 levels over the Phanerozoic Eon as a whole (PMCC = +0.12). For smectite formed during weathering processes, this behavior suggests control through Equation 1. Decreasing atmospheric CO_2 levels are potentially associated with less acidic weathering conditions correspond-

ing to increased values of activity ratios such as $(a_{Mg^{2+}})/(a_{H^+})^2$, which favor smectites relative to illite-group minerals if the Mg-contents of the smectites are higher than those of illite. Despite progress in the thermodynamic characterization of these minerals (Vidal and Dubacq 2009; Dubacq et al. 2010), the compositions of the Russian platform clays are not known, which hampers more quantitative evaluations of the stability of smectite relative to illite.

This scenario, in which clay mineral formation links to atmospheric CO_2 , requires that atmospheric CO_2 levels control CO_2 concentrations in the weathering zone, which is not the case in the present day (CO_2 partial pressures in modern soil zones are typically much higher than in the atmosphere). However, in the early Phanerozoic Eon, atmospheric CO_2 levels could have directly controlled CO_2 concentrations in the shallow subsurface. Before the rise and spread of deeply rooted vascular land plants about 350 to 300 Ma ago, the partial pressure of CO_2 in the soil zone was significantly lower than at present (owing to fewer respiratory processes) and thus more directly responsive to the level of CO_2 in the atmosphere (Berner 2004). Consequently, a decrease of atmospheric CO_2 resulted in a CO_2 decrease in the soil zone, lower acidity, and more smectite relative to illite. After ~350 Ma, deep root activity and associated biological activity (e.g., AMF) resulted in greater levels of CO_2 respiration in the soil zone. In turn, this biological processing resulted in CO_2 concentrations in the soil zone that were not directly controlled by atmospheric CO_2 levels.

Figure 5 offers tentative support for the above arguments; namely, the negative correlation of smectite-group minerals and CO_2 levels is particularly strong from 550 to about 350 Ma; however, after ~300 Ma the correlation appears weaker. A new pattern of smectite abundances may have emerged between ~200 Ma and the present in terms of O_2 instead of CO_2 . The relative abundance of smectite-group minerals during the last 200 Ma increases directly with O_2 levels, as would be expected based on the rise of EMF discussed above. Increasing O_2 in the presence of EMF facilitated oxidation reactions, thereby favoring the formation of Fe^{3+} -bearing smectites at the expense of chlorite-group minerals (and presumably other mafic minerals, e.g., Sugimori et al. 2008).

Relative illite abundances correlate with CO_2 levels (Fig. 6; PMCC = +0.69) but not with O_2 levels (PMCC = +0.13). Although significant illite must have formed by the well-documented process of smectite diagenesis (Fig. 1), the correlation with CO_2 levels over hundreds of millions of years suggests a strong influence of the weathering environment on illite formation as well. The correlation is consistent with the notion discussed above that lower CO_2 levels favor lower acidity and less illite relative to smectite. It is also plausible that the rise of terrestrial plant life from the Silurian Period through the end of the Permian Period might have caused an increased demand for K^+ in soil and weathering zones, which contributed to destabilizing illite relative to kaolinite-group minerals (Knoll and James 1987). Recent studies have suggested that illite may be stabilized in the uppermost parts of modern soil zones, but this stabilization depends on the development of abundant decayed surface organic matter such as leaf litter (Barre et al. 2009). In the early to mid-Paleozoic Era, the near-surface soil zone could

have been quite different (Knoll and James 1987; Berner 2004).

Overall, the relative abundances of kaolinite- and chlorite-group minerals show negative and positive correlations, respectively, with O₂ levels, whereas smectite- and illite-group minerals show negative and positive correlations, respectively, with CO₂ levels. Within these overall correlations, changes in the patterns of the correlations suggest that relative clay mineral abundances are sensitive indicators of major biological events relevant to the weathering zone, including the rise of deep-rooted vascular plants and their associated mycorrhizal fungi. These correlations point to the viability of mineralogical proxies for paleo-atmospheric compositions, and they emphasize the tightly linked nature of the evolution of Earth's biosphere, atmosphere, and minerals deep into geologic time (Hazen et al. 2008; Sverjensky and Lee 2010).

CLAY MINERAL EVOLUTION ON MARS

In contrast to Earth, recent observations have shown that the ancient surface of Mars contains a diversity of clay minerals, most of which are thought to be more than 3 billion years old (Poulet et al. 2005; Bibring et al. 2006; Mustard et al. 2008; Ehlmann et al. 2009, 2010; Milliken et al. 2009; Carter et al. 2010; Milliken and Bish 2010), although it is as yet unresolved whether these clay minerals represent primarily surface/near-surface processes (e.g., weathering, diagenesis, precipitation from fluids) or subsurface hydrothermal processes (Poulet et al. 2005; Tosca and Knoll 2009; Ehlmann et al. 2011; Meunier et al. 2012). Paradoxically, we may have much to learn about the lost evolutionary record of clay minerals on early Earth by studying their surviving counterparts in the ancient (and largely preserved) rock record of Mars.

The successful landing of NASA's Curiosity rover in Gale Crater, coupled with observations from earlier lander, rover, and orbiter missions, provides an opportunity for comparing clay mineral evolution on Earth and Mars. Of the several modes of clay mineral paragenesis on Earth described in this study, the earliest—subsurface aqueous/hydrothermal alteration—has unambiguously occurred on Mars (Griffith and Shock 1997; Poulet et al. 2005; Bibring et al. 2006; Mustard et al. 2008; Ehlmann et al. 2011; Meunier et al. 2012). The alteration of basalt and other crustal mafic lithologies to trioctahedral ferromagnesian clay minerals must have commenced early in the Pre-Noachian (>4.1 Ga) history of Mars and may continue to this day in deep hydrothermal zones. Strong evidence from regional mineralogical surveys also points to possible authigenic clay mineral formation in martian sediments (Chevrier et al. 2007; Murchie et al. 2009; Milliken et al. 2009), including possible authigenesis by high-temperature fluids associated with intrusive bodies (Meunier et al. 2012).

Significant evidence has accumulated that suggests Mars had abundant surface and near-surface water during its first half- to one-billion years, making it likely that a suite of authigenic clay minerals and products of water-rock interactions formed in the sediments associated with these ancient bodies of water. The timing, extent, and duration of a warm, wet martian surface environment are less certain (Squyres and Kasting 1994; Ehlmann et al. 2011). The clay minerals detected at the martian surface are found predominantly in terrains that are dated to the Noachian Eon (>3.5 Ga) based on crater counts,

consistent with this time period being favorable for clay mineral formation if the clays in these deposits are detrital (Poulet et al. 2005; Mustard et al. 2008; Murchie et al. 2009). However, the ages of these clay minerals would be relatively unconstrained if they are instead authigenic, as they could have formed later than the rocks in which they are contained. In contrast, younger (Hesperian-aged) terrains are characterized by the presence of sulfate salts and a paucity of clay minerals.

This apparent mineralogical dichotomy has led to the hypothesis that Mars experienced a dramatic climatic change that is directly recorded in the mineralogy of martian strata (Bibring et al. 2006). Unlike Earth, which has experienced an increase in the diversity and production of clay minerals through time, the martian crust may record the opposite. Alternatively, martian clay minerals may not reflect conditions in the near-surface environment if they instead formed deep in the crust or are the products of magmatic processes (Ehlmann et al. 2011; Meunier et al. 2012).

Unraveling the physical and chemical weathering processes on Mars is, by necessity, quite difficult. Data returned by the Spirit, Opportunity, and Curiosity rovers currently provide the best in situ geochemical and mineralogic information. Specifically, recent X-ray diffraction data acquired by the CheMin instrument on the Curiosity rover have confirmed the presence of clay minerals on Mars in rock powder collected by a drill from what has been classified as a mudstone (http://www.nasa.gov/mission_pages/msl/news/msl20130312.html; accessed 04/12/2013). These clay minerals and other associated minerals and elements indicate formation in circum-neutral pH fluids. This formation environment is in contrast to those previously explored by the Opportunity and Spirit rovers, which, coupled with laboratory experiments, suggest acidic conditions, iron oxidation, and low water-to-rock ratios dominating surface chemical weathering over the past several billion years of Mars' history (Hurowitz and McLennan 2007; Tosca et al. 2009; Altheide et al. 2010; Hurowitz et al. 2010). Such conditions are not favorable to extensive clay formation, in direct opposition to orbital observations of clay mineral deposits in the oldest (Noachian) terrains on Mars. The presence of a putative ancient northern ocean on Mars or a more vigorous hydrologic cycle in the first billion years would alleviate some of these discrepancies, and Curiosity's in situ observations of the clay minerals reported in Gale crater from orbital data (Milliken et al. 2010) will continue to provide new insight into water-rock interactions on ancient Mars.

A fourth association of near-surface clay minerals on Earth is related to the exposure of low-grade, chlorite-bearing metamorphic rocks (greenschist facies) through plate tectonics processes. Plate tectonics is not active on Mars, although Yin (2012) suggested the existence of large-scale strike-slip faulting in Valles Marineris on Mars. However, asteroid impacts may have played a role in excavating clay-bearing formations of deep crustal origin (Fairén et al. 2010; Ehlmann et al. 2011). In addition, asteroid impacts may have played an indirect role in the formation of clays through the generation of deep hydrothermal zones in the vicinity of impact craters (Newsom 1980; Rathbun and Squyres 2002; Abramov and Kring 2005; Schwenzer and Kring 2009; Marzo et al. 2010). Intriguingly,

the vast majority of clay minerals detected from orbit thus far on Mars do not require high-temperature conditions to form. Instead, smectites, mixed-layer chlorite/smectite, and chlorite-group minerals appear to be the dominant phases and may indicate temperatures <100 °C, although occurrences of prehnite and serpentine have been reported in some locations (Ehlmann et al. 2009, 2011). In the early history of Mars, impacts into a water-bearing crust would surely have produced clay minerals, and the same was likely true for Earth at that time. However, the extent to which such martian clays were altered, recycled, or exposed by erosion and later impacts remains to be determined.

Based on this analysis, the diversity and relative abundances of clay minerals on Mars likely differ from Earth in several significant ways. On Mars, with a global basaltic crust and minimal granitization, trioctahedral ferromagnesian clay minerals will occur more abundantly than dioctahedral Al-Fe³⁺ species. Furthermore, dioctahedral ferric species will dominate over those of Al, at least if the clays formed at the surface. Conditions of the shallow subsurface on Mars are likely to be more reducing, suggesting that Fe²⁺ will predominate over Fe³⁺ varieties.

The diversity of clay mineral species is likely to be significantly less than on Earth—perhaps limited to the 25 species suggested to occur in stage 2 and 3 environments (Tables 1 and 2). Minerals associated with Li, Zn, Ni, Cu, and Cr enrichment (through volumetrically extensive fluid-rock interaction) and subsequent weathering and secondary alteration processes on Earth are less likely to occur on Mars. By the same token, minor and trace element distributions of clay minerals on Mars are likely to differ significantly from those on Earth.

Finally, there is as yet no evidence for microbially-induced clay mineral formation, much less the modes of biological weathering associated with the rise of a terrestrial biosphere—processes associated with stage 10 of Earth's clay mineral evolution. An important open question is whether any combination of clay minerals might represent a convincing biomarker. Summons et al. (2011) identified several biosignatures that could potentially be identified using the instruments on the Curiosity rover. These potential biomarkers include organism morphologies, biofabrics, diagnostic organic molecules, isotopic signatures, evidence of biomineralization and bioalteration, spatial patterns in chemistry, and biogenic gases. They considered biogenic organic molecules and biogenic atmospheric gases to be most definitive and most readily detectable by the SAM instrument on MSL.

Beyond these differences in clay mineral diversity, relative abundances, and extent, a fascinating and as yet unresolved question relates to the differences in clay mineral preservation on Earth vs. Mars. On Earth there is a paucity of clays >1 Ga, but on Mars the majority of clay minerals appear to date from the planet's first billion years. These differences can be ascribed in part to the recycling of Earth's clay minerals through subduction, as well as the destruction of clay minerals through thermal metamorphism and possibly dehydration by CO₂-rich fluids (Janardhanan et al. 1979; Newton et al. 1980; Peterson and Newton 1989; Santosh et al. 1990). Nevertheless, it remains an open question why we find so few Archean clay minerals on Earth even in relatively unaltered sedimentary basins (e.g., Tosca and Knoll 2009).

CONCLUDING REMARKS

Of the more than 4800 known minerals on Earth, only a few dozen are classified as clay minerals, yet these species have played a major role in the evolution of Earth's near-surface environment throughout our planet's history. The four-billion-year rock record on Earth provides scant direct evidence of clay mineral diversification and increased distribution through geologic time, particularly for its first three billion years. Nevertheless, observations of more recent clay-bearing formations, coupled with our growing knowledge of the modes of clay paragenesis, provide a sound basis for understanding clay mineral evolution. Thus, it appears that the variety and volume of clay minerals present at Earth's surface has increased dramatically since planetary accretion.

This overview of clay mineral evolution has focused on the appearance of new clay mineral species and groups, with hints regarding the changing distributions and volumes of those crustal phases. However, the most revealing changes in clay mineralogy through Earth history may be related to as yet unrecognized compositional variations, including trace and minor element compositions, as well as their isotopic subtleties. The effects of Earth's evolving near-surface environment, including variations in redox conditions; atmospheric, ocean, and groundwater geochemistry; tectonic processes, notably associated with orogenic activity; and the origin of life and subsequent evolution of marine and terrestrial ecosystems; must be reflected in chemical variations that have been little studied. Future work will undoubtedly shed additional light on the remarkable effects of biological activity on Earth's near-surface mineralogy, and the continuing co-evolution of the geosphere and biosphere.

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