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PALEOMINERALOGY OF THE HADEAN EON: A PRELIMINARY SPECIES LIST

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*“By the way, were there any clay minerals in the Archean?”
Harold Morowitz, December 6, 2006*

ABSTRACT. The Hadean Eon, encompassing Earth’s first 550 million years, was a time of significant planetary evolution. Nevertheless, prebiotic Earth’s near-surface environment may have held no more than approximately 420 different rock-forming or accessory mineral species that were widely distributed and/or volumetrically significant. This relative Hadean mineralogical parsimony is a consequence of the limited modes of mineral paragenesis prior to 4 Ga compared to the last 3.0 billion years. Dominant Hadean Eon mineralizing processes include the evolution of a diverse suite of intrusive and extrusive igneous lithologies; hydrothermal alteration over a wide temperature range, notably serpentinization; authigenesis in marine sediments; diagenesis and low-grade metamorphism in near-surface environments; and impact-related processes, including shock mineralization, creation of marginal hydrothermal zones, and excavation of deep metamorphosed terrains. On the other hand, the Hadean Eon may have been notably lacking in mineralization generated by plate tectonic processes, such as subduction zone volcanism and associated fluid-rock interactions, which result in massive sulfide deposition; convergent boundary orogenesis and consequent extensive granitoid-rooted continental landmasses; and the selection and concentration of incompatible elements in complex pegmatites, with hundreds of accompanying minerals. The dramatic mineralogical consequences of life are reflected in the absence of Hadean biomineralization; for example, the lack of extensive carbonate deposits and the associated restricted development of skarn and cave minerals prior to 4 Ga. Most importantly, it was not until after the establishment via photosynthesis of significant near-surface redox gradients that supergene alteration, redox-controlled ore deposition, and subaerial weathering in an oxidizing environment could diversify Earth’s near-surface mineralogy. These post-Hadean processes may be responsible for over 4000 of the more than 4800 approved mineral species. Any scenario for life’s origins that invokes minerals as agents of molecular synthesis, selection, protection, or organization must take into account the limited mineralogical repertoire of the time.

Key words: Mineral evolution, clay minerals, impact processes, geochemistry, origin of life, prebiotic chemistry, serpentinization, crust, redox state

INTRODUCTION

The character and diversity of Earth’s near-surface mineralogy has evolved dramatically over 4.567 billion years. A succession of physical, chemical, and biological processes has transformed the initially homogeneous dust and gas of the solar nebula into increasingly differentiated zones of varied temperature, pressure, and composi-

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tion. Recent studies exploring aspects of Earth's "mineral evolution" point to key events in the mineralogical diversification of our planet, notably the accretion and differentiation of Earth with an extensive basaltic veneer and hydrosphere; the initiation of granite formation and the associated formation of complex pegmatites; the establishment of the plate tectonics cycle, with subduction and consequent mineralization associated with arc volcanism and orogenesis; the formation of continents and subsequent appearances of evaporite and weathering minerals, as well as associated marginal sedimentary wedges; and the origin and evolution of life, with eventual profound mineralogical influences on the chemistry of the oceans and atmosphere (Hazen and others, 2008, 2009, 2011, 2012, 2013a, 2013b; Grew and Hazen, 2009, 2010a, 2010b; Hazen and Ferry, 2010; Papineau, 2010; Grew and others, 2011; Golden and others, 2013).

Estimates of the timing of these processes remain uncertain, but it seems likely that widespread granitization, plate tectonics, extensive continent formation, and the origin of life all postdated the Hadean Eon (>4.03 Ga). An important conclusion of mineral evolution investigations, therefore, is that the mineralogical inventory of early Earth was far more restricted than today. Given that many models of life's geochemical origins rely on minerals for such varied roles as selection, concentration, protection, organization, and catalysis (Bernal, 1951; Goldschmidt, 1952; Lahav and others, 1978; Cairns-Smith and Hartmann, 1986; Wächtershäuser, 1988a; Summers and Chang, 1990; Ferris and Ertem, 1992; Lahav, 1994, 1999; Russell and Hall, 1997; Orgel, 1998; Smith, 1998; Cody and others, 2000, 2004; Ricardo and others, 2004; Hazen, 2005, 2006; Deamer, 2011), it is important to document what rock-forming and common accessory mineral species might have been present at 4 Ga—the approximate time when life is thought to have emerged.

The principal objective of this paleomineralogy contribution is to present a preliminary list of mineral species that were likely to be widely distributed and/or volumetrically significant at or near Earth's surface ~ 4 billion years ago. Note that the imposition of these two selection criteria related to the relative extent of plausible Hadean minerals—distribution and volume—deviate from previous mineral evolution studies, which cited any mineral occurrence, including reports of isolated micro- or nano-phase minerals. Here, however, the objective is to catalog phases that might have played a significant role in Hadean geochemical processes, including prebiotic chemical evolution and the origins of life. Consequently, more than 100 minerals identified as rare and volumetrically minor meteorite constituents are not included in the preliminary list.

Tables 1 and 2 list 420 proposed minerals—tabulations that might serve as a starting point for future discussions of Hadean mineralogical diversity. This effort employs strategies of both inclusion and exclusion. First, the list includes minerals through examination of the primary mineralogy of meteorites (stages 1 and 2 of mineral evolution) and the meager surviving rock record of Earth's first billion years (stage 3). In addition, the presence or absence of other potential minerals is inferred through geochemical, petrologic, tectonic, and crystal chemical arguments. In particular, any mineral that is restricted in its paragenesis to stages 4 through 10 of mineral evolution (Hazen and others, 2008), including those minerals that first appeared as a consequence of subduction-related processes and back-arc volcanism, orogenesis associated with plate tectonics, complex pegmatite formation derived from S-type granites, continent-scale terrestrial processes such as evaporation of inland seas, or biomineralization and other biologically-mediated processes, is unlikely to have been present to any significant extent during the Hadean Eon and is thus excluded from tables 1 and 2.

TABLE 1

Preliminary species list for predicted Hadean Eon (>4.03 Ga) silicate minerals, chemical formulas, and modes of occurrence. The following International Mineralogical Association (IMA) recognized minerals fulfill criteria given in the text for rock-forming minerals, and include widespread and/or volumetrically significant accessory phases

Name	IMA Formula	Occurrences*
<u>Silica</u>		
Coesite	SiO ₂	HP, IM
Cristobalite	SiO ₂	CM, HY, MA, MT
Moganite	SiO ₂ ·nH ₂ O	HY
Opal	SiO ₂ ·nH ₂ O	HY
Quartz	SiO ₂	GR, HY, MT, SD, ZR
Stishovite	SiO ₂	HP, IM
Tridymite	SiO ₂	AK, CM, HY, MT, VP
<u>Garnets</u>		
Almandine	Fe ²⁺ ₃ Al ₂ (SiO ₄) ₃	GR, RM, SD
Andradite	Ca ₃ Fe ³⁺ ₂ (SiO ₄) ₃	AK, CM, MT, RM
Grossular	Ca ₃ Al ₂ (SiO ₄) ₃	CM, MT, RM
Hibschite	Ca ₃ Al ₂ (SiO ₄) _{3-x} (OH) _{4x} (x=0.2-1.5)	AK, LT
Majorite	Mg ₃ (Fe ²⁺ , Si) ₂ (SiO ₄) ₃	IM
Pyrope	Mg ₃ Al ₂ (SiO ₄) ₃	MA, SP, RM, UM
Schorlomite	Ca ₃ (Ti ⁴⁺ , Fe ³⁺) ₂ [(Si, Fe ³⁺)O ₄] ₃	AK, CM
Spessartine	Mn ²⁺ ₃ Al ₂ (SiO ₄) ₃	CM, GR, MN
Uvarovite	Ca ₃ Cr ₂ (SiO ₄) ₃	CM, HY, SP
<u>Olivines and M²⁺₂SiO₄ Polymorphs</u>		
Fayalite	Fe ²⁺ ₂ SiO ₄	AK, GR, UM
Forsterite	Mg ₂ SiO ₄	CM, MA, MT, UM, UR
Kirschsteinite	CaFe ²⁺ SiO ₄	AK, CM, MT
Larnite	Ca ₂ SiO ₄	CM
Monticellite	CaMgSiO ₄	CM, MT, RM
Ringwoodite	Mg ₂ SiO ₄	IM, MT
Tephroite	Mn ²⁺ ₂ SiO ₄	CM, MN, RM
Wadsleyite	Mg ₂ SiO ₄	IM, MT
Willemite	Zn ₂ SiO ₄	RM
<u>Feldspars, Feldspathoids, and Sodalite Group</u>		
Albite	NaAlSi ₃ O ₈	AK, GR, HY, LT, MT, SD, ZR
Anorthite	CaAl ₂ Si ₂ O ₈	CM, HP, MA, MT, RM
Cancrinite	(Na, Ca, □) ₈ (Al ₆ Si ₆)O ₂₄ (CO ₃ , SO ₄) ₂ ·2H ₂ O	AK
Haüyne	Na ₃ Ca(Si ₃ Al ₃)O ₁₂ (SO ₄)	AK
Kalsilite	KAlSiO ₄	AK
Lazurite	Na ₃ Ca(Si ₃ Al ₃)O ₁₂ S	CM
Leucite	K(Si ₂ Al)O ₆	AK, MA, UM
Marialite	3NaAlSi ₃ O ₈ □NaCl	CM, HY, RM
Meionite	(Ca, Na) ₄ (Si, Al) ₁₂ O ₂₄ (CO ₃ , SO ₄ , Cl)	CM, HY, RM
Microcline	KAlSi ₃ O ₈	AK, GR, RM, SD
Nepheline	NaAlSiO ₄	AK, MA, MT
Nosean	Na ₈ (Si ₆ Al ₆)O ₂₄ (SO ₄)·H ₂ O	AK
Orthoclase	KAlSi ₃ O ₈	GR, MA, SD, UM, ZR
Sanidine	KAlSi ₃ O ₈	CM, GR, HY, MA
Sodalite	Na ₄ Si ₃ Al ₃ O ₁₂ Cl	AK, HY, MT
<u>Zeolites</u>		
Analcime	Na(Si ₂ Al)O ₆ ·H ₂ O	AU, HY, MA
Apophyllite-(KOH)	KCa ₄ Si ₈ O ₂₀ (OH, F)·8H ₂ O	HY, MA
Chabazite-Ca	Ca ₂ Al ₄ Si ₈ O ₂₄ ·13H ₂ O	HY, MA
Chabazite-K	(K ₂ NaCa _{0.5})Al ₄ Si ₈ O ₂₄ ·11H ₂ O	HY, MA
Chabazite-Na	(Na ₃ K)Al ₄ Si ₈ O ₂₄ ·11H ₂ O	HY, MA
Cowlesite	Ca(Al ₂ Si ₃)O ₁₀ ·5-6H ₂ O	HY, MA
Epistilbite	Ca ₃ (Si ₁₈ Al ₆)O ₄₈ ·16H ₂ O	HY, MA
Erionite-Ca	Ca ₅ (Si ₂₆ Al ₁₀)O ₇₂ ·28H ₂ O	HY, MA
Garronite	NaCa _{2.5} (Si ₁₀ Al ₆)O ₃₂ ·13H ₂ O	HY, MA

TABLE 1
(continued)

Name	IMA Formula	Occurrences*
<u>Zeolites (cont)</u>		
Gismondine	$\text{Ca}_2(\text{Si}_4\text{Al}_4)\text{O}_{16} \cdot 8\text{H}_2\text{O}$	HY, MA
Gmelinite-Na	$\text{Na}_4(\text{Si}_8\text{Al}_4)\text{O}_{24} \cdot 11\text{H}_2\text{O}$	HY, MA
Gonnardite	$(\text{Na},\text{Ca})_2(\text{Si},\text{Al})_5\text{O}_{10} \cdot 3\text{H}_2\text{O}$	AK, HY, MA
Heulandite-Ca	$\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 24\text{H}_2\text{O}$	HY, MA
Heulandite-K	$\text{KCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 24\text{H}_2\text{O}$	HY, MA
Laumontite	$\text{Ca}(\text{Si}_4\text{Al}_2)\text{O}_{12} \cdot 4\text{H}_2\text{O}$	AU, HY, MA
Mesolite	$\text{Na}_2\text{Ca}_2(\text{Si}_9\text{Al}_6)\text{O}_{30} \cdot 8\text{H}_2\text{O}$	HY, MA
Mordenite	$(\text{Na}_2,\text{Ca},\text{K}_2)_4(\text{Al}_8\text{Si}_{40})\text{O}_{96} \cdot 28\text{H}_2\text{O}$	AU, HY, MA
Natrolite	$\text{Na}_2(\text{Si}_3\text{Al}_2)\text{O}_{10} \cdot 2\text{H}_2\text{O}$	AK, GR, HY, MA
Offretite	$\text{KCaMg}(\text{Si}_{13}\text{Al}_3)\text{O}_{36} \cdot 15\text{H}_2\text{O}$	HY, MA
Pectolite	$\text{NaCa}_2\text{Si}_3\text{O}_7(\text{OH})$	AK, HY, MA, SP
Phillipsite-Ca	$\text{Ca}_3(\text{Si}_{10}\text{Al}_6)\text{O}_{32} \cdot 12\text{H}_2\text{O}$	AU, HY, MA
Phillipsite-K	$\text{K}_6(\text{Si}_{10}\text{Al}_6)\text{O}_{32} \cdot 12\text{H}_2\text{O}$	AU, HY, MA
Scolecite	$\text{Ca}(\text{Si}_3\text{Al}_2)\text{O}_{10} \cdot 3\text{H}_2\text{O}$	AK, HY, MA
Stellerite	$\text{Ca}_4(\text{Si}_{28}\text{Al}_8)\text{O}_{72} \cdot 28\text{H}_2\text{O}$	HY, MA
Stilbite-Ca	$\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 28\text{H}_2\text{O}$	HY, MA
Thomsonite-Ca	$\text{NaCa}_2(\text{Al}_3\text{Si}_5)\text{O}_{20} \cdot 6\text{H}_2\text{O}$	AK, AU, HY, MA
Wairakite	$\text{Ca}(\text{Si}_4\text{Al}_2)\text{O}_{12} \cdot 2\text{H}_2\text{O}$	HY
Yugawaralite	$\text{Ca}(\text{Si}_6\text{Al}_2)\text{O}_{16} \cdot 4\text{H}_2\text{O}$	HY
<u>Pyroxenes and Pyroxenoids</u>		
Aegirine	$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$	AK, AU, HY, RM
Aegirine-Augite	$(\text{Ca},\text{Na})(\text{Fe}^{3+},\text{Mg},\text{Fe}^{2+})\text{Si}_2\text{O}_6$	AK, RM
Augite	$(\text{Ca},\text{Mg},\text{Fe})_2\text{Si}_2\text{O}_6$	MA, MT, RM, UM
Bustamite	$\text{CaMn}^{2+}\text{Si}_2\text{O}_6$	CM, MN
Clinoestatite	MgSiO_3	MA, MT, UM
Clinoferrosilite	$\text{Fe}^{2+}\text{SiO}_3$	MA, UM
Diopside	$\text{CaMgSi}_2\text{O}_6$	CM, MA, MT, RM, UM
Enstatite	MgSiO_3	MA, MT, RM, UM
Ferrosilite	$\text{Fe}^{2+}_2(\text{SiO}_3)_2$	RM
Hedenbergite	$\text{CaFe}^{2+}\text{Si}_2\text{O}_6$	CM, GR, MT, RM
Johannsenite	$\text{CaMn}^{2+}\text{Si}_2\text{O}_6$	CM, HY, MN
Omphacite	$(\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})\text{Si}_2\text{O}_6$	HP, MA
Pigeonite	$(\text{Mg},\text{Fe},\text{Ca})\text{SiO}_3$	MA, MT, RM
Pyroxmangite	$\text{Mn}^{2+}\text{SiO}_3$	LT, MN, RM
Rhodonite	$\text{Mn}^{2+}\text{SiO}_3$	CM, HY, MN, RM
Wollastonite	CaSiO_3	CM, MT
<u>Amphiboles</u>		
Actinolite	$\text{Ca}_2(\text{Mg},\text{Fe}^{2+})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$	CM, MA, RM, UM
Anthophyllite	$\square\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	MA, RM, UM
Arfvedsonite	$\text{NaNa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$	AK, GR
Barroisite	$\square\text{NaCa}[\text{Mg}_3\text{Al}_2](\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	RM
Cummingtonite	$\square\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	MA, RM
Eckermannite	$\text{NaNa}_2(\text{Mg}_4\text{Al})\text{Si}_8\text{O}_{22}(\text{OH})_2$	AK
Edenite	$\text{NaCa}_2\text{Mg}_5(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	MA, RM
Ferro-actinolite	$\square\text{Ca}_2\text{Fe}^{2+}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	RM
Ferro-edenite	$\text{NaCa}_2\text{Fe}^{2+}_5(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	AK, RM
Ferrohornblende	$\square\text{Ca}_2(\text{Fe}^{2+}_4\text{Al})(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	GR, MA
Ferropargasite	$\text{NaCa}_2(\text{Fe}^{2+}_4\text{Al})(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$	RM
Ferrichterite	$\text{Na}_2\text{CaFe}^{2+}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	AK, GR
Gedrite	$\square\text{Mg}_5\text{Al}_2(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$	CM, RM
Grunerite	$\square\text{Fe}^{2+}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	CM, RM
Hastingsite	$\text{NaCa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})(\text{Si}_6\text{Al}_2)\text{O}_{22}(\text{OH})_2$	AK, GR, RM
Kaersutite	$\text{NaCa}_2(\text{Mg}_4\text{Ti})(\text{Si}_6\text{Al}_2)\text{O}_{22}\text{O}(\text{OH})_2$	AK, MA
Katophorite	$\text{NaNaCa}[\text{Fe}^{2+}_4(\text{Al},\text{Fe}^{3+})](\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$	AK, HP
Magnesian-arfvedsonite	$\text{NaNa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$	AK, CM, RM
Magnesian-hastingsite	$\text{NaCa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$	MA
Magnesian-hornblende	$\square\text{Ca}_2[\text{Mg}_4(\text{Al},\text{Fe}^{3+})]\text{Si}_7\text{AlO}_{22}(\text{OH})_2$	GR, RM, ZR

TABLE 1
(continued)

Name	IMA Formula	Occurrences*
<u>Amphiboles (cont)</u>		
Magnesiokatophorite	NaNaCa(Mg ₄ Al)(Si ₇ Al)O ₂₂ (OH) ₂	AK
Magnesioriebeckite	□Na ₂ (Mg ₃ Fe ³⁺) ₂ Si ₈ O ₂₂ (OH) ₂	RM
Manganocummingtonite	□Mn ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	MN, RM
Manganogrunerite	□Mn ₂ Fe ²⁺ ₅ Si ₈ O ₂₂ (OH) ₂	CM, MN, RM
Pargasite	NaCa ₂ (Mg ₄ Al)(Si ₆ Al ₂)O ₂₂ (OH) ₂	CM, MA, RM, UM
Richterite	Na ₂ CaMg ₅ Si ₈ O ₂₂ (OH) ₂	AK, CM, MT
Riebeckite	□Na ₂ (Fe ²⁺ ₃ Fe ³⁺) ₂ Si ₈ O ₂₂ (OH) ₂	AK, GR
Tremolite	□Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	CM, RM
Tschermakite	□Ca ₂ (Mg ₃ AlFe ³⁺)Si ₆ Al ₂ O ₂₂ (OH) ₂	RM, UM
Winchite	□NaCa(Mg ₄ Al)Si ₈ O ₂₂ (OH) ₂	RM
<u>Micas</u>		
Annite	KFe ²⁺ ₃ (Si ₃ Al)O ₁₀ (OH) ₂	GR, RM
Celadonite	KMgFe ³⁺ Si ₄ O ₁₀ (OH) ₂	GR, LT, MA
Clintonite	CaAlMg ₂ (SiAl ₃)O ₁₀ (OH) ₂	CM, RM
Margarite	CaAl ₂ (Si ₂ Al ₂)O ₁₀ (OH) ₂	RM
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	AU, GR, HY, RM, ZR
Paragonite	NaAl ₃ (Si ₃ Al)O ₁₀ (OH) ₂	LT, RM
Phlogopite	KMg ₃ (Si ₃ Al)O ₁₀ (OH) ₂	AK, CM, GR, HY, MA, RM, UM, ZR
Siderophyllite	KFe ²⁺ ₂ Al(Si ₂ Al ₂)O ₁₀ (OH) ₂	AK, GR
<u>Clay Minerals</u>		
Amesite	Mg ₂ Al(SiAl)O ₅ (OH) ₄	LT
Antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄	CM, HY, UM
Beidellite	(Na,Ca) _{0.3} Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ •nH ₂ O	HY
Berthierine	(Fe ²⁺ , Fe ³⁺ , Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄	AU, HY, MT
Caryopilite	(Mn ²⁺) ₃ Si ₂ O ₅ (OH) ₄	MN, RM
Chamosite	(Fe ²⁺ , Mg, Al, Fe ³⁺) ₆ (Si,Al) ₄ O ₁₀ (OH, O) ₈	AU
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	HY, MA, MT, SP, UM
Clinochlore	Mg ₆ Si ₄ O ₁₀ (OH) ₈	CM, HY, MT, RM
Corrensite	(Ca, Na, K) ₁₋₃ (Mg, Fe, Al) ₉ (Si, Al) ₈ O ₂₀ (OH) ₁₀ •nH ₂ O	AU, HY
Cronstedtite	(Fe ²⁺ , Fe ³⁺) ₃ (Si, Fe ³⁺) ₂ O ₅ (OH) ₄	LT, HY, MT
Dickite	Al ₂ Si ₂ O ₅ (OH) ₄	AU, HY
Fraipontite	(Zn, Al) ₃ (Si, Al) ₂ O ₅ (OH) ₄	HY
Greinalite	(Fe ²⁺ , Fe ³⁺) ₂₋₃ Si ₂ O ₅ (OH) ₄	AU, MT
Halloysite-7Å	Al ₂ Si ₂ O ₅ (OH) ₄	HY
Halloysite-10Å	Al ₂ Si ₂ O ₅ (OH) ₄ •2H ₂ O	HY
Hydrobiotite	K(Mg, Fe ²⁺) ₆ (Si, Al) ₈ O ₂₀ (OH) ₄ •nH ₂ O	AU
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	HY
Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	HY, SP
Minnesotaite	(Fe ²⁺) ₃ Si ₄ O ₁₀ (OH) ₂	RM
Montmorillonite	(Na, Ca) _{0.3} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •nH ₂ O	HY, LT, MT
Nacrite	Al ₂ Si ₂ O ₅ (OH) ₄	HY
Népouite	Ni ₃ Si ₂ O ₅ (OH) ₄	HY
Nontronite	Na _{0.3} Fe ³⁺ ₂ (Si, Al) ₄ O ₁₀ (OH) ₂ •nH ₂ O	AU, CM, HY
Pecoraite	Ni ₃ Si ₂ O ₅ (OH) ₄	HY, MT, UM
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	HY, LT
Rectorite	(Na, Ca)Al ₄ (Si, Al) ₈ O ₂₀ (OH) ₄ •2H ₂ O	HY, LT
Saponite	(Ca, Na) _{0.3} (Mg, Fe ²⁺) ₃ (Si, Al) ₄ O ₁₀ (OH) ₂ •4H ₂ O	HY, MT
Sauconite	Na _{0.3} Zn ₃ (Si, Al) ₄ O ₁₀ (OH) ₂ •4H ₂ O	HY
Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂ •6H ₂ O	AU, HY
Sudoite	Mg ₂ Al ₃ (Si ₃ Al)O ₁₀ (OH) ₈	AU, HY, LT
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	AU, HY, LT, MT
Tosudite	Na _{0.5} (Al, Mg) ₆ (Si, Al) ₈ O ₁₈ (OH) ₁₂ •5H ₂ O	AU, HY
Vermiculite	Mg _{0.7} (Mg, Fe ³⁺ , Al) ₆ (Si, Al) ₈ O ₂₀ (OH) ₄ •8H ₂ O	HY, UM
<u>Miscellaneous Silicates</u>		
Aenigmatite	Na ₄ (Fe ²⁺ ₁₀ Ti ₂)O ₄ [Si ₁₂ O ₃₆]	AK, MT
Afwillite	Ca ₃ (SiO ₄)(SiO ₂ (OH) ₂)•2H ₂ O	CM
Åkermanite	Ca ₂ MgSi ₂ O ₇	AK, CM, MT

TABLE 1
(continued)

Name	IMA Formula	Occurrences*
Miscellaneous Silicates (cont)		
Alleghanyite	$Mn^{2+}_5(SiO_4)_2(OH)_2$	HY, MN
Allophane	$Al_2O_3(SiO_2)_{1.3-2.0} \cdot 2.5-3.0H_2O$	LT, HY
Andalusite	Al_2SiO_5	CM, GR, RM, SD
Babingtonite	$Ca_2Fe^{2+}Fe^{3+}Si_5O_{14}(OH)$	CM, GR
Bementite	$Mn_7Si_6O_{15}(OH)_8$	CM, MN
Braunite	$Mn^{2+}Mn^{3+}_6SiO_{12}$	MN, RM
Carpholite	$Mn^{2+}Al_2Si_2O_6(OH)_4$	LT, MN
Caryopilite	$(Mn^{2+})_3Si_2O_5(OH)_4$	CM, MN
Chloritoid	$Fe^{2+}Al_2OSiO_4(OH)_2$	HY, RM
Chondrodite	$Mg_5(SiO_4)_2F_2$	AK, CM
Clinohumite	$Mg_9(SiO_4)_4F_2$	AK, CM, RM
Clinozoisite	$Ca_2Al_3(Si_2O_7)(SiO_4)O(OH)$	CM, RM
Cordierite	$Mg_2Al_4Si_5O_{18}$	CM, GR, HP, MA, RM
Cuspidine	$Ca_4Si_2O_7F_2$	CM
Dravite	$NaMg_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3OH$	MA, RM, SD
Epidote	$Ca_2Fe^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$	CM, RM
Eudialyte	$Na_{12}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	AK, GR, VP
Friedelite	$Mn^{2+}_8Si_6O_{15}(OH)_{10}$	RM, MN
Ganophyllite	$(K,Na)_x(Mn^{2+},Al,Mg)_6(Si,Al)_{10}O_{24}(OH)_4 \cdot nH_2O$ (x=1-2; n=7-11)	RM, MN
Gehlenite	$Ca_2Al(SiAl)O_7$	CM, MT, UM
Gyrolite	$NaCa_{16}(Si_{23}Al)O_{60}(OH)_8 \cdot 14H_2O$	HY
Humite	$Mg_7(SiO_4)_3(F,OH)_2$	AK, CM
Ilvaite	$CaFe^{3+}Fe^{2+}_2O(Si_2O_7)(OH)$	CM, RM
Inesite	$Ca_2Mn^{2+}_7Si_{10}O_{28}(OH)_2 \cdot 5H_2O$	HY, MN
Kyanite	Al_2OSiO_4	HP, RM, SD
Lorenzenite	$Na_2Ti_2O_3(Si_2O_6)$	AK
Mullite	$Al_{4-2x}Si_{2-2x}O_{10-x}$ (x~0.4)	RM
Murmanite	$Na_2Ti_2(Si_2O_7)O_2 \cdot 2H_2O$	AK, HY
Neotocite	$(Mn^{2+},Fe^{2+})SiO_3 \cdot H_2O$	HY, MN
Norbergite	$Mg_3SiO_4F_2$	CM
Okenite	$Ca_{10}Si_{18}O_{46} \cdot 18H_2O$	MA
Osumilite	$KFe^{2+}_2(Al_5Si_{10})O_{30}$	CM, GR
Osumilite-Mg	$KMg(Al_5Si_{10})O_{30}$	RM
Ottrelite	$Mn^{2+}Al_2O(SiO_4)(OH)_2$	HY, MN, RM
Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH) \cdot 4H_2O$	LT
Parsettensite	$(K,Na,Ca)_7.5(Mn,Mg)_{49}Si_{72}O_{168}(OH)_{50} \cdot nH_2O$	MN
Piemontite	$Ca_2Mn^{3+}Al_2(Si_2O_7)(SiO_4)O(OH)$	LT, MN, RM
Prehnite	$Ca_2Al(Si_3Al)O_{10}(OH)_2$	GR, HY, LT, MA
Pumpellyite-Fe ²⁺	$Ca_2Fe^{2+}Al_2(SiO_4)(Si_2O_7)(OH)_2 \cdot H_2O$	CM
Pumpellyite-Mg	$Ca_2MgAl_2(SiO_4)(Si_2O_7)(OH)_2 \cdot H_2O$	LT
Roedderite	$KNaMg_2(Mg_3Si_{12})O_{30}$	CM, MT
Rhönite	$Ca_4(Mg_8Fe^{3+}_2Ti_2)O_4[Si_6Al_6O_{36}]$	AK, CM, MA, MT
Sapphirine	$Mg_4(Mg_3Al_9)O_4[Si_3Al_9O_{36}]$	MA, MT, RM
Schorl	$NaFe^{2+}_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3OH$	HY, RM, SD
Sekaninaite	$Fe^{2+}_2Al_4Si_5O_{18}$	GR, LT
Sérandite	$NaMn^{2+}_2Si_3O_8(OH)$	AK, CM
Sillimanite	Al_2OSiO_4	RM, SD
Sonolite	$Mn^{2+}_9(SiO_4)_4(OH)_2$	MN, RM
Spurrite	$Ca_5(SiO_4)_2(CO_3)$	CM
Staurolite	$Fe^{2+}_2Al_9Si_4O_{23}(OH)$	HP, RM, SD
Stilpnomelane	$(K,Ca,Na)(Fe,Mg,Al)_8(Si,Al)_{12}(O,OH)_{36} \cdot nH_2O$	RM
Sursassite	$Mn^{2+}_2Al_3(SiO_4)(Si_2O_7)(OH)_3$	LT, MN
Tacharanite	$Ca_{12}Al_2Si_{18}O_{33}(OH)_{36}$	HY, MA
Thorite	$ThSiO_4$	GR, SD, ZR
Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	CM

TABLE 1
(continued)

Name	IMA Formula	Occurrences*
Miscellaneous Silicates (cont)		
Titanite	CaTiSiO_5	AK, CM, GR, RM, SD, ZR
Tobermorite	$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	CM, HY
Topaz	$\text{Al}_2\text{SiO}_4\text{F}_2$	GR, HY, RM, SD
Ussingite	$\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$	AK, HY
Vesuvianite	$(\text{Ca},\text{Na})_{19}(\text{Al},\text{Mg},\text{Fe})_{13}(\text{SiO}_4)_{10}(\text{Si}_2\text{O}_7)_4(\text{OH},\text{F},\text{O})_{10}$	AK, CM, MA, SP, UM
Xonotlite	$\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$	CM, SP
Zircon	ZrSiO_4	GR, MA, MT, RM, SD
Zoisite	$\text{Ca}_2\text{Al}_3(\text{Si}_2\text{O}_7)(\text{SiO}_3)\text{O}(\text{OH})$	HP, RM

* Modes of Occurrence: AK = alkali igneous; AU = authigenic; CM = contact metamorphism; GR = granitoid igneous; HP = high-pressure metamorphism; HY = hydrothermal alteration; IM = shock high-pressure phase; LT = low-temperature metamorphism; MA = mafic igneous; MN = manganese deposits; MT = meteorite; RM = regional metamorphism; SD = clastic sedimentary environment; SP = serpentinization; UM = ultramafic igneous; UR = "ur-mineral" in pre-solar grains; VP = vapor phase deposition and volcanic fumaroles; ZR = inclusions in Hadean zircons.

OBSERVED HADEAN MINERALS

A modest rock record survives from Earth's earliest billion years in the form of meteorites (Papike, 1998) and scattered Eoarchean (4.03-3.6 Ga) and possibly Hadean (>4.03 Ga) outcrops (Bowring and Williams, 1999; Furnes and others, 2007; O'Neil and others, 2008; Papineau, 2010). These specimens point to a limited but varied Hadean mineralogical inventory, which includes most of the rock-forming minerals known today, albeit in differing proportions. The first step in establishing Hadean mineral diversity, therefore, is to enumerate the surviving mineralogy from presolar processes and the first three stages of Earth's mineral evolution (Hazen and others, 2008).

The "Ur-Minerals"

Cosmic mineralogy began with the formation of approximately a dozen "ur-minerals" that condensed during cooling and expansion of the gaseous envelopes of supernovas and red giant stars (tables 1 and 2). Hazen and others (2008) proposed that diamond was the first mineral, as a consequence of its high temperature of crystallization (~4400 °C) and the abundance of carbon in stellar atmospheres of massive stars. Diamond was followed by condensation of graphite (C), moissanite (SiC), the nitrides osbornite and nierite (TiN and Si₃N₄, respectively), rutile (TiO₂), corundum (Al₂O₃), spinel (MgAl₂O₄), hibonite (CaAl₁₂O₁₉), forsterite (Mg₂SiO₄), and enstatite (MgSiO₃), which have also been identified in pre-solar dust grains (Nittler, 2003; Mostefaoui and Hoppe, 2004; Messenger and others, 2006; Vollmer and others, 2007). These refractory minerals all form from the most abundant products of nucleosynthesis and all possess condensation temperatures above ~1900 °C. All of these crystalline phases have been present continuously throughout star-forming regions of the cosmos since the first hundred million years following the Big Bang (Hazen and others, 2008; Hazen, 2012).

Stages 1 and 2—Meteorite Minerals

Meteorites record the earliest history of the solar nebula, from the initial processing of presolar dust and gas, through successive stages of heating, condensation, accretion, differentiation, and alteration. More than 250 mineral species have been identified thus far in meteorites (Rubin, 1997a, 1997b; Brearley and Jones, 1998;

TABLE 2

Predicted Hadean Eon (>4 Ga) non-silicate minerals, chemical formulas, and modes of occurrence. The following International Mineralogical Association (IMA) recognized minerals fulfill criteria given in the text for rock-forming and widespread accessory phases

Name	IMA Formula	Occurrences*
<u>Native Elements and Alloys</u>		
Arsenic	As	HY
Awaruite	Ni ₃ Fe	MT, SP
Copper	Cu	HY, MA, MT
Diamond	C	HP, IM, MT, UR, ZR
Gold	Au	HY, SD
Graphite	C	GR, HY, MA, MT, RM, UM, UR, ZR
Iron	Fe	MA, MT, VP
Lead	Pb	HY
Lonsdaleite	C	IM, MT, UR
Nickel	Ni	SP, UM
Platinum	Pt	HY, MA, SD, UM
Silver	Ag	HY
Sulphur	S	VP
Taenite	(Ni,Fe)	MT, SP
Tetrataennite	FeNi	MT
Wairauite	CoFe	MT, SP
Zinc	Zn	HY, VP
<u>Carbides, Nitrides, Phosphides and Silicides</u>		
Carlsbergite	CrN	MT
Cohenite	Fe ₃ C	MA, MT, UM
Haxonite	(Fe,Ni) ₂₃ C ₆	MT
Khamrabaevite	(Ti,V,Fe)C	MT, UM
Moissanite	SiC	HP, MT, UR
Nickelphosphide	Ni ₃ P	MT
Nierite	Si ₃ N ₄	MT, UR
Osbornite	TiN	MT, UM, UR
Perryite	(Ni,Fe) ₈ (Si,P) ₃	MT
Schreibersite	(Fe,Ni,Cr) ₃ P	MT
Suessite	(Fe ₃ Si)	MT
<u>Sulfides, Arsenides, and Sulfosalts</u>		
Acanthite	Ag ₂ S	HY
Alabandite	MnS	LT, MN, MT
Anilite	Cu ₇ S ₄	HY
Arsenopyrite	FeAsS	HY, LT, RM
Bornite	Cu ₅ FeS ₄	CM, HY, MA
Brezinaite	Cr ₃ S ₄	MT
Caswellsilverite	NaCrS ₂	MT
Chalcocite	Cu ₂ S	HY
Chalcopyrite	CuFeS ₂	HY, MA, MT
Cinnabar	HgS	HY
Covellite	CuS	HY
Cubanite	CuFe ₂ S ₃	HY, MT
Daubr�elite	Fe ²⁺ Cr ₂ S ₄	MT
Digenite	Cu _{11.8} S	HY, MA, VP
Djerfisherite	K ₆ (Fe,Cu,Ni) ₂₅ S ₂₆ Cl	CM, HY, MA, MT, UM
Djurleite	Cu ₃₁ S ₁₆	HY
Enargite	Cu ₃ AsS ₄	HY, LT
Galena	PbS	HY, CM
Gersdorffite	NiAsS	HY
Greigite	Fe ₃ S ₄	AU, HY
Hauerite	MnS ₂	LT
Heazlewoodite	Ni ₃ S ₂	HY, MT, SP, UM
L�llingite	FeAs ₂	HY
Mackinawite	(Fe,Ni) _{1+x} S (x = 0-0.07)	HY, MT, SP

TABLE 2
(continued)

Name	IMA Formula	Occurrences*
<u>Sulfides, Arsenides, and Sulfosalts (cont)</u>		
Marcasite	FeS ₂	HY, LT
Maucherite	Ni ₁₁ As ₈	HY
Millerite	NiS	LT, SP
Molybdenite	MoS ₂	HY
Nickeline	NiAs	HY, UM
Nickelskutterudite	NiAs ₂₋₃	HY
Ninningerite	MgS	MT
Oldhamite	CaS	MT
Orpiment	As ₂ S ₃	LT, VP
Pararammelsbergite	NiAs ₂	HY
Pentlandite	(Ni,Fe) ₉ S ₈	HY, MT, UM
Polydymite	Ni ₃ S ₄	HY
Pyrite	FeS ₂	CM, HY, LT, MA, RM, UM, ZR
Pyrrhotite	Fe ₇ S ₈	HY, MA, MT
Rammelsbergite	NiAs ₂	HY
Realgar	AsS	LT, VP
Sphalerite	ZnS	HY, LT, MT
Tennantite	Cu ₁₂ As ₄ S ₁₃	CM, HY
Tochilinite	6(Fe _{0.9} S) ₅ [(Mg,Fe)(OH) ₂]	MT, SP, UM
Troilite	FeS	MT, SP, UM
Valleriite	2[(Fe,Cu)S]·1.53[(Mg,Al)(OH) ₂]	HY, SP, UM
Violarite	Fe ²⁺ Ni ³⁺ ₂ S ₄	HY
Wurtzite	ZnS	HY, LT
<u>Halides</u>		
Bischofite	MgCl ₂ ·6H ₂ O	EV, LT
Carnalite	KMgCl ₃ ·6H ₂ O	EV, LT
Cryolite	Na ₃ AlF ₆	AU, GR, VP
Fluorite	CaF ₂	AK, GR, HY, LT, VP
Halite	NaCl	EV
Prosopite	CaAl ₂ (F,OH) ₈	GR
Ralstonite	Na _{0.5} (Al,Mg) ₂ (F,OH) ₆ ·H ₂ O	GR, HY
Salammoniac	NH ₄ Cl	VP
Sellaite	MgF ₂	EV, GR, RM, VP
Sylvite	KCl	EV, VP
Villiaumite	NaF	AK, EV
<u>Oxides and Hydroxides</u>		
Anatase	TiO ₂	HY, SD
Baddeleyite	ZrO ₂	MA, UM
Bixbyite	Mn ³⁺ ₂ O ₃	MN, RM
Böhmite	AlO(OH)	HY, LT
Brookite	TiO ₂	CM, HY, RM, SD
Brucite	Mg(OH) ₂	HY, LT, SP
Cassiterite	SnO ₂	CM, GR, HY, SD
Chromite	Fe ²⁺ Cr ₂ O ₄	MT, UM
Corundum	Al ₂ O ₃	AK, CM, HY, MT, RM, SD, UR
Diaspore	AlO(OH)	HY, LT
Ferrihydrite	Fe ³⁺ ₄₋₅ (OH, O) ₁₂	LT, MT
Franklinite	ZnFe ³⁺ ₂ O ₄	CM, MN, RM
Gahnite	ZnAl ₂ O ₄	GR, RM, SD
Galaxite	Mn ²⁺ Al ₂ O ₄	MN, RM
Geikielite	MgTiO ₃	CM, SD, SP, UM
Gibbsite	Al(OH) ₃	LT
Goethite	Fe ³⁺ O(OH)	LT
Grossite	CaAl ₄ O ₇	CM, MT
Groutite	Mn ³⁺ O(OH)	HY
Hausmannite	Mn ²⁺ Mn ³⁺ ₂ O ₄	HY, MN, RM

TABLE 2
(continued)

Name	IMA Formula	Occurrences*
Oxides and Hydroxides (cont)		
Hematite	$\text{Fe}^{3+}_2\text{O}_3$	CM, GR, HY, RM, VP
Hercynite	$\text{Fe}^{2+}\text{Al}_2\text{O}_4$	MA, MT, RM, SD, UM
Hetaerolite	$\text{ZnMn}^{3+}_2\text{O}_4$	HY, MN
Hibonite	$(\text{Ca,Ce})(\text{Al,Ti,Mg})_{12}\text{O}_{19}$	MT, RM, UR
Ice	H_2O	VP
Ilmenite	$\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$	GR, MA, MT, RM, SD, UM
Jacobsite	$\text{Mn}^{2+}\text{Fe}^{3+}_2\text{O}_4$	HY, MN
Lepidocrocite	$\text{Fe}^{3+}\text{O}(\text{OH})$	LT
Magnesiocromite	$\text{MgCr}^{3+}_2\text{O}_4$	MA, SD, SP, UM
Magnesioferrite	$\text{MgFe}^{3+}_2\text{O}_4$	IM, MA, MT, RM, UM, VP
Magnetite	$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$	CM, GR, MA, MT, RM, SD, UM
Manganite	$\text{Mn}^{3+}\text{O}(\text{OH})$	LT, MN
Manganosite	Mn^{2+}O	LT
Nordstrandite	$\text{Al}(\text{OH})_3$	AK, LT
Periclase	MgO	CM, MT, RM
Perovskite	CaTiO_3	AK, MT
Portlandite	$\text{Ca}(\text{OH})_2$	CM, LT, VP
Pridelite	$(\text{K,Ba})(\text{Ti}^{4+},\text{Fe}^{3+},\text{Mg})_8(\text{O,OH})_{16}$	AK, UM
Pyrochroite	$\text{Mn}^{2+}(\text{OH})_2$	LT, MN
Pyrophanite	$\text{Mn}^{2+}\text{TiO}_3$	GR, RM, SP
Rutile	TiO_2	CM, GR, HY, MA, MT, RM, SD, UR, ZR
Spinel	MgAl_2O_4	CM, MA, RM, SD, UM, UR
Thorianite	ThO_2	MA, SP, UM
Todorokite	$(\text{Na,Ca,K,Ba,Sr})_{1-x}(\text{Mn,Mg,Al})_6\text{O}_{12}\cdot 3-4\text{H}_2\text{O}$	HY, MN, VP
Ulvöspinel	$\text{Fe}^{2+}_2\text{TiO}_4$	MA, MT
Uraninite	UO_2	AK, GR, HY, SD
Wüstite	Fe^{2+}O	HP, MA, MT, RM
Zincite	ZnO	RM
Zirconolite	$(\text{Ca,Y})\text{Zr}(\text{Ti,Mg,Al})_2\text{O}_7$	AK, MT, UM
Carbonates**		
Alumohydrocalcite	$\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O}$	LT, SP
Ankerite	$\text{CaFe}(\text{CO}_3)_2$	AU, HY, RM
Aragonite	CaCO_3	EV, HP, HY, MA, PR
Artinite	$\text{Mg}_2\text{CO}_3(\text{OH})_2\cdot 3\text{H}_2\text{O}$	LT, SP
Calcite	CaCO_3	AK, HY, MA, MT, PR
Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	AK, HY
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	CM, HY, MT, PR, UM
Dypingite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$	SP
Gaylussite	$\text{Na}_2\text{Ca}(\text{CO}_3)_2\cdot 5\text{H}_2\text{O}$	AK, EV
Huntite	$\text{CaMg}_3(\text{CO}_3)_4$	HY, LT, PR, SP
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 4\text{H}_2\text{O}$	HY, PR, SP
Hydrotalcite	$\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$	HY, SP
Kutnohorite	$\text{CaMn}^{2+}(\text{CO}_3)_2$	LT, MN
Magnesite	MgCO_3	EV, HY, LT, MT, RM, SP
Monohydrocalcite	$\text{CaCO}_3\cdot \text{H}_2\text{O}$	EV, HY, PR
Nahcolite	NaHCO_3	AK, EV, PR
Natron	$\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$	AK, EV, PR
Nesquehonite	$\text{MgCO}_3\cdot 3\text{H}_2\text{O}$	LT, SP
Rhodochrosite	MnCO_3	AU, CM, HY, LT, MN
Shortite	$\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$	AK, MA, PR, UM
Siderite	FeCO_3	AK, AU, GR, HY, UM
Strontianite	SrCO_3	HY
Thermonatrite	$\text{Na}_2\text{CO}_3\cdot \text{H}_2\text{O}$	EV, HY, VP
Trona	$\text{Na}_3(\text{HCO}_3)(\text{CO}_3)\cdot 2\text{H}_2\text{O}$	EV, VP
Vaterite	CaCO_3	LT
Witherite	BaCO_3	HY

TABLE 2
(continued)

Name	IMA Formula	Occurrences*
Sulfates***		
Alum-K	$KAl(SO_4)_2 \cdot 12H_2O$	EV
Aluminite	$Al_2SO_4(OH)_4 \cdot 7H_2O$	LT, VP
Alunite	$KAl_3(SO_4)_2(OH)_6$	LT
Alunogen	$Al_2(SO_4)_3(H_2O)_{12} \cdot 5H_2O$	LT, VP
Anhydrite	$CaSO_4$	EV, HY, LT, VP
Barite	$BaSO_4$	HY
Bassanite	$CaSO_4 \cdot 0.5H_2O$	EV, LT, VP
Celestine	$SrSO_4$	HY, MA, PR
Epsomite	$MgSO_4 \cdot 7H_2O$	EV, MT
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	CM, LT
Glauberite	$Na_2Ca(SO_4)_2$	EV, MA, VP
Gypsum	$CaSO_4 \cdot 2H_2O$	EV, LT, MT, PR, VP
Kieserite	$MgSO_4 \cdot H_2O$	EV, VP
Langbeinite	$K_2Mg_2(SO_4)_3$	EV
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	EV, HY, VP
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$	AU, HY
Picromerite	$K_2Mg(SO_4)_2 \cdot 6H_2O$	EV, HY, VP
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$	EV, LT, VP
Syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$	EV, HY, VP
Tamarugite	$NaAl(SO_4)_2 \cdot 6H_2O$	VP
Thénardite	Na_2SO_4	EV, VP
Phosphates		
Beusite	$Mn^{2+}Fe^{2+}_2(PO_4)_2$	MT
Childrenite	$Fe^{2+}AlPO_4(OH)_2 \cdot H_2O$	HY
Chlorapatite	$Ca_5(PO_4)_3Cl$	CM, MA, MT, ZR
Farringtonite	$Mg_3(PO_4)_2$	MT
Fluorapatite	$Ca_5(PO_4)_3F$	AK, CM, GR, HY, MA, RM, SD
Galileite	$NaFe^{2+}_4(PO_4)_3$	MT
Graftonite	$(Fe^{2+}, Mn^{2+}, Ca)_3(PO_4)_2$	MT
Hydroxylapatite	$Ca_5(PO_4)_3OH$	HY, SP
Johnsomervilleite	$Na_{10}Ca_6Mg_{18}Fe^{2+}_{25}(PO_4)_{36}$	MT
Merrillite	$Ca_9NaMg(PO_4)_7$	MT
Monazite-Ce	$CePO_4$	AK, GR, MA, SD
Sarcopside	$Fe^{2+}_3(PO_4)_2$	MT
Stanfieldite	$Ca_4Mg_5(PO_4)_6$	MT
Triplite	$(Mn^{2+}, Fe^{2+})_2PO_4(F, OH)$	HY
Wagnerite	Mg_2PO_4F	RM
Wavellite	$Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$	HY
Whitlockite	$Ca_9Mg(PO_4)_6(PO_3OH)$	MT

* Modes of Occurrence: AK = alkali igneous; AU = authigenic; CM = contact metamorphism; EV = evaporite; GR = granitoid igneous; HP = high-pressure metamorphism; HY = hydrothermal alteration; IM = shock high-pressure phase; LT = low-temperature metamorphism; MA = mafic igneous; MN = manganese deposits; MT = meteorite; PR = aqueous precipitate; RM = regional metamorphism; SD = clastic sedimentary environment; SP = serpentinization; UM = ultramafic igneous; UR = "ur-minerals" from pre-solar grains; VP = vapor phase deposition at volcanic fumaroles and other pneumatolytic processes; ZR = inclusions in Hadean zircons.

** See also the silicate-carbonates spurrite and tilleyite in table 1.

*** See also the silicate-sulfide minerals of the sodalite group in table 1.

Papike, 1998; Krot and others, 2006; Brearley, 2006; MacPherson, 2007); therefore, these minerals have been a persistent feature of the near-surface environment of Earth and other terrestrial planets and moons for more than 4.5 billion years.

The number of confirmed meteorite minerals continues to grow thanks to the diligent examination of numerous specimens with microbeam techniques. More than

150 trace mineral phases have been documented in isolated micro- or nano-scale grains, in many instances from a single meteorite specimen (for example, Fuchs and Blander, 1977; Lovering and others, 1979; Armstrong and others, 1987; Caillet Komorowski and others, 2009, 2010). However, the focus here is only on the most widely distributed and/or volumetrically significant rock-forming and accessory minerals. In tables 1 and 2, 104 meteorite phases (38 silicates and 66 non-silicates) are listed that are sufficiently common in meteorites that they might be invoked in any robust scenario of early Earth and the origin of life. All other documented meteorite mineral phases are rare and volumetrically minor.

Framework silicates.—A variety of framework silicates has been reported from meteorites (for example, Brearley and Jones, 1998; Mittlefehldt and others, 1998); however, only 7 mineral species—the SiO_2 polymorphs cristobalite, quartz, and tridymite; the plagioclase feldspars albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$); the feldspathoid nepheline (NaAlSiO_4); and sodalite ($\text{Na}_4\text{Si}_3\text{Al}_3\text{O}_{12}\text{Cl}$)—are well represented and thus included in table 1. Calcic plagioclase is particularly abundant, both in chondrites (in chondrules and calcium aluminum inclusions, or CAIs) and in a variety of achondrites. Rare or unconfirmed framework silicates based on isolated reports of the barium feldspar celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$; Wasserberg and others, 1977), zeolites (Woltzka and Wark, 1982), or the scapolite group mineral marialite [$\text{Na}_4(\text{Al}_3\text{Si}_9\text{O}_{24})\text{Cl}$; Alexander and others, 1987] are not included.

Orthosilicates.—Forsterite (Mg_2SiO_4) typically containing >90 atomic percent of the Mg end-member is among the commonest mineralogical constituents of meteorites. It is a ubiquitous component of most chondrites and achondrites, and is the dominant silicate mineral in brachinites (olivine cumulates with up to 98% olivine; Nehru and others, 1992) and ureilites, as well as pallasites and a variety of other iron meteorites (Mittlefehldt and others, 1998). The Mg-Ca olivine monticellite (CaMgSiO_4) occurs in calcium-aluminum inclusions (CAIs) in a number of chondrites. Though rare in most other types of meteorites, the Ca- Fe^{2+} olivine kirschsteinite ($\text{CaFe}^{2+}\text{SiO}_4$) is a significant accessory mineral in the angrite group of achondrites.

Additional relatively common calcic orthosilicates in CAIs include the calcic garnets andradite [$\text{Ca}_3\text{Fe}^{3+}_2(\text{SiO}_4)_3$] and grossular [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$] and the melilite group minerals åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and gehlenite [$\text{Ca}_2\text{Al}(\text{SiAl})\text{O}_7$]. Zircon (ZrSiO_4) occurs in the HED group of achondrites, while the high-pressure shock polymorphs of olivine—ringwoodite and wadsleyite (both Mg_2SiO_4)—are relatively common, if microscopic, accessory minerals.

Chain silicates.—Magnesium and calcium chain silicates are found in most meteorites. The (Mg,Fe^{2+}) SiO_3 pyroxenes clinoenstatite, (ortho)enstatite, and pigeonite, typically with $\text{Mg}/\text{Fe} > 3$, occur to some extent in almost all meteorites, and near end-member enstatite (En_{99}) accounts for more than 95 volume percent of some aubrites, which are essentially MgSiO_3 cumulates. The calcic clinopyroxenes augite [$(\text{Ca},\text{Mg},\text{Fe})_2\text{Si}_2\text{O}_6$] and diopside ($\text{CaMgSi}_2\text{O}_6$), and to a lesser extent hedenbergite ($\text{CaFe}^{2+}\text{Si}_2\text{O}_6$), are common constituents of the CAIs and chondrules in chondrites, as well as a wide variety of achondrites. Amphiboles, notably richterite [$\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$] and the pyroxenoid wollastonite (CaSiO_3), constitute additional rare and volumetrically minor chain silicate phases in meteorites.

Layer silicates.—The matrices of many primitive CI chondrites are dominated (>50 to 60%) by clay minerals, including Mg-Fe members of the serpentine group and saponite [$(\text{Ca},\text{Na})_{0.3}(\text{Mg},\text{Fe}^{2+})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], with minor chlorite (Brearley and Prinz, 1992). Mg-Fe serpentine group minerals, including cronstedtite [$(\text{Fe}^{2+}_2\text{Fe}^{3+})_3(\text{Si},\text{Fe}^{3+})_2\text{O}_5(\text{OH})_4$], chrysotile [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$], and greenalite [$(\text{Fe}^{2+},\text{Fe}^{3+})_{2.3}\text{Si}_2\text{O}_5(\text{OH})_4$], and a 7-A chlorite group mineral, possibly berthierine [$(\text{Fe}^{2+},\text{Fe}^{3+},\text{Al})_3(\text{Si},\text{Al})_2\text{O}_5(\text{OH})_4$], 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). Saponite is also a common constituent of the altered matrix of CV and CR chondrites, while secondary alteration of CAIs in CV-type chondrites results in montmorillonite $[(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and possibly serpentine and saponite (Tomeoka and Buseck, 1990). 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).

Metals, carbides, nitrides, silicides, and phosphides.—The mineralogy of many meteorites is distinguished from that of Earth's near-surface environment today by the occurrence of a number of highly reduced phases (table 2; see also table 2 *et sequentia* in Mittlefehldt and others, 1998). Dominant among these minerals are the metal alloys of iron, including awaruite (Ni_3Fe), native iron (Fe), taenite (Ni,Fe), tetrataenite (FeNi), and wairuite (CoFe). Note that the commonly cited meteorite mineral "kamecite" (Fe,Ni) is now considered to be a variety of native iron and thus is not an approved IMA mineral species. Meteorites host a number of fascinating carbide minerals, most abundantly moissanite (SiC) and cohenite (Fe_3C), but also haxonite $[(\text{Fe,Ni})_{23}\text{C}_6]$ and khamrabaevite $[(\text{Ti,V,Fe})\text{C}]$.

Distinctive mineralogical features of some highly reduced meteorites, including enstatite chondrites, are the phosphides nickelphosphide (Ni_3P), perryite $[(\text{Ni,Fe})_8(\text{Si,P})_3]$, and schreibersite $[(\text{Fe,Ni,Cr})_3\text{P}]$ and the nitrides carlsbergite (CrN), nierite (Si_3N_4), and osbornite (TiN)—the latter two phases also being among the ur-minerals. Schreibersite is particularly abundant in some iron meteorites; thus, this reactive phase has been invoked in models of the prebiotic phosphorus cycle and key chemical steps in biogenesis (Pasek and others, 2007; Pasek, 2008). The silicide suessite (Fe_3Si) is an uncommon accessory in some iron meteorites. Additional extremely rare iron silicides, possibly associated with extraterrestrial materials but not listed in table 2, include gupeite (Fe_3Si), hapkeite (Fe_2Si), linzhilite (FeSi_2), luobusaite ($\text{Fe}_{0.84}\text{Si}_2$), naquite (FeSi), xifengite (Fe_5Si_3), and zangboite (TiFeSi_2). These phases, though individually scarce, demonstrate the collective availability of extremely reduced, and therefore potentially reactive, mineral phases in the Hadean near-surface environment.

Sulfides.—Sulfide minerals are ubiquitous secondary phases in meteorites. The Fe sulfides pyrrhotite (Fe_7S_8) and troilite (FeS) are most common, but at least a dozen other Fe, Ni, Cu, Cr, and Zn sulfides have been documented (table 2), along with such frequently reported oddities as alabandite (MnS), caswellsilverite (NaCrS_2), niningerite (MgS), and oldhamite (CaS).

An important question with regard to meteorite sulfides, as well as many other mineral groups, is the role of rare elements in meteorite mineralization. In particular, the least differentiated chondrite meteorites incorporate more than 80 stable chemical elements, yet most of those elements are not expressed in the guise of separate minerals. It is unclear whether most rare elements are incorporated into other minerals through solid solution, or remain widely dispersed (for example along grain boundaries), or form as yet unrecognized nanophases. Reports of micron-scale meteorite grains of molybdenite (MoS_2 ; Fuchs and Blander, 1977) and metacinnabar (HgS; Caillet Komorowski and others, 2009, 2010) point to the latter possibility. However, these phases are neither sufficiently widespread nor volumetrically significant to constitute important prebiotic meteorite minerals.

Oxides.—At least 15 oxide minerals (in addition to the SiO_2 polymorphs discussed under framework silicates above) are commonly found in meteorites. Corundum (Al_2O_3), periclase (MgO), rutile (TiO_2), and wüstite (Fe^{2+}O) are all widespread oxide phases. The commonest ABO_3 oxides are ilmenite ($\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$) and perovskite

(CaTiO₃), which are often observed in CAIs. Of special importance are the spinel group minerals chromite (Fe²⁺Cr₂O₄), hercynite (Fe²⁺Al₂O₄), magnesioferrite (MgFe³⁺₂O₄), magnetite (Fe²⁺Fe³⁺₂O₄), spinel (MgAl₂O₄), and ulvöspinel (Fe²⁺₂TiO₄). Spinel group minerals form extensive solid solutions among these end-members. Also of interest is the iron oxide-hydroxide ferrihydrite [Fe³⁺₄₋₅(OH,O)₁₂], which is found in association with clay minerals and is formed by aqueous alteration.

As with sulfides, a complete inventory of reported meteoritic oxides includes several scarce phases of relatively rare elements that have been observed exclusively as micron-scale grains in a few samples. Baddelyite (ZrO₂; Lovering and others, 1979), coulsonite (FeV₂O₄; Armstrong and others, 1987), and thorianite (ThO₂; Lovering and others, 1979), for example, are not present in sufficient abundance to constitute significant prebiotic meteorite phases.

Sulfates, carbonates, and phosphates.—Sulfates are extremely rare in meteorites. The only widespread meteoritic sulfates are gypsum (CaSO₄ · 2H₂O) and epsomite (MgSO₄ · 7H₂O), which occur as alteration products, for example of melilite group minerals in some chondrites.

Few carbonate minerals have been reported from meteorites, though secondary carbonate minerals in veins and isolated matrix grains constitute as much as 5 volume percent of some CI chondrites. Calcite (CaCO₃), dolomite [CaMg(CO₃)₂], and magnesite (MgCO₃) are the only widespread phases. Isolated reports of minor aragonite (CaCO₃), rhodochrosite (MnCO₃), and siderite (FeCO₃) suggest that these minerals do not play a significant role in meteorites.

Phosphate minerals are widely reported but generally rare in meteorites. At least 15 species have been recorded, of which 10 (table 2) have been confirmed from multiple meteorite samples (Brearley and Jones, 1998; Mittlefehldt and others, 1998; Sugiura and Hoshino, 2003; Grew and others, 2010). These phases are of special interest as prebiotic repositories of the essential biological element phosphorus. Chlorapatite [Ca₅(PO₄)₃Cl] and whitlockite [Ca₉Mg(PO₄)₆(PO₃OH)] are the most common meteoritic phosphates, occurring in a wide range of chondrite and achondrite types. Type IIIAB iron meteorites incorporate beusite [(Mn²⁺Fe²⁺)₂(PO₄)₂], galileite [NaFe²⁺₄(PO₄)₃], graffonite [(Fe²⁺,Mn²⁺,Ca)₃(PO₄)₂], johnsomervilleite [Na₁₀Ca₆Mg₁₈Fe²⁺₂₅(PO₄)₃₆], and sarcopsidite [(Fe²⁺)₃(PO₄)₂]. In addition, pallasites often hold whitlockite, stanfieldite [Ca₄Mg₅(PO₄)₆], and farringtonite [Mg₃(PO₄)₂], while merrillite [Ca₉NaMg(PO₄)₇] is found in some chondrites.

Stage 3—Evolution of Igneous Rocks (4.55-4.03 Ga)

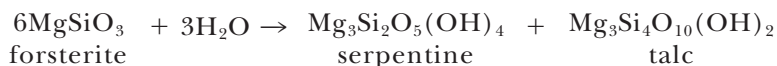
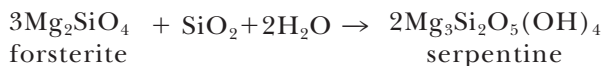
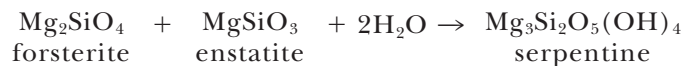
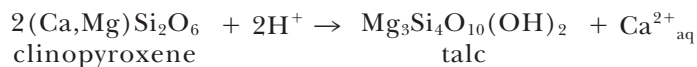
The third stage of Earth's mineral evolution commenced immediately following planetary accretion with a protracted interval of igneous rock differentiation. Earth's crustal evolution was abruptly halted by the Moon-forming impact of Theia and consequent formation of a globe-encircling magma ocean at $\sim 4.53 \pm 0.2$ Ga (Tonks and Melosh, 1993; Ruzicka and others, 1999; Touboul and others, 2007). Subsequent global volcanism and associated outgassing of mantle volatiles produced a dynamic hydrosphere, possibly with globe-spanning shallow oceans by 4.4 Ga (Wilde and others, 2001). The evolution of igneous rocks resumed rapidly as varied processes, including fractional crystallization, crystal settling, assimilation reactions, and extensive volcanism and degassing led to element fractionation and the production of increasingly Si- and alkali-rich magmas (Bowen, 1928; Yoder, 1976, 1979). Within Earth's first half-billion years, a diverse suite of igneous rocks had appeared, including peridotite and other ultramafic lithologies, representing undifferentiated mantle; basalt, gabbro, amphibolite, and a host of other mafic lithologies derived from the partial melting of peridotite; and increasingly differentiated alkali-rich igneous rocks, including syenites, monzonites, and feldspathoid-rich rocks. Partial melting of basalt and other mafic rocks produced the important silica-enriched tonalite-trondhjemite-granodiorite (TTG)

series of granitoid rocks, which are significantly less dense than peridotite or basalt and thus formed the roots of growing continental landmasses.

Mineralogy surviving from the Eoarchean Era.—Papineau (2010) reviewed the probable dominant lithologies in Hadean Earth's earliest crust, and tabulated their associated major and accessory minerals based on the known Eoarchean Era rock record. Tables 1 and 2 list 179 minerals, including 116 silicate and 63 nonsilicate species likely to have occurred as primary minerals in ultramafic, mafic, alkali, and granitoid igneous rocks prior to 4 Ga.

Additional insight to Hadean Eon mineralogy may be provided by inclusions in the most ancient zircon grains—those older than 4 Ga. More than a dozen major and minor minerals have been documented in Hadean zircons (Trail and others, 2004; Hopkins and others, 2008, 2010; Papineau, 2010; tables 1 and 2). These phases bear a striking resemblance to minerals preserved in Eoarchean TTG-derived gneisses, and are thus thought to reflect those host lithologies. Note, however, that Rasmussen and others (2011) have questioned whether these included minerals are in fact older than the host zircon crystals.

Hydrothermal alteration and metamorphism.—Additional mineralogical diversity in the Hadean Eon arose from extensive metamorphism and hydrothermal alteration of the crust. Serpentinization, by which hydrothermal fluids altered the dominant ultramafic and mafic lithologies of the first crust, led to at least 31 mineral species (Schrenk and others, 2013; tables 1 and 2). Notably, a suite of predominantly trioctahedral ferromagnesian clay and hydroxide minerals must have been present in Earth's near-surface environment from the earliest Hadean Eon as a consequence of serpentinization reactions. Characteristic clay-forming alteration reactions of olivine and pyroxenes (Deer and others, 1962; Harder, 1972; Fontanaud and Meunier, 1983; Newman, 1987; Nozaka and others, 2008) include:



The hydrothermal alteration of ferromagnesian minerals is often characterized by a clay mineral sequence with progressively decreasing Mg/Si; for example, serpentinized olivine may later be replaced first by vermiculite, then mixed-layer saponite-talc and saponite (Velde, 1985; Nozaka and others, 2008). Note that a comparable suite of trioctahedral clay minerals has been detected in the ancient crust of Mars believed to have formed during this time period (for example, Poulet and others, 2005; Bibring and others, 2006; Mustard and others, 2008; Milliken and others, 2009; Carter and others, 2010; Ehlmann and others, 2010, 2011; Milliken and Bish, 2010).

Hydrothermal alteration and low-temperature, regional and contact metamorphism also might have resulted in extensive and varied assemblages of more than 300 Hadean minerals (many of which display multiple modes of paragenesis), as listed in tables 1 and 2. These processes, which significantly diversified Earth's near-surface

mineralogy prior to 4 Ga, led to new suites of zeolites, clay minerals, sulfides, sulfates, carbonates, and phosphates.

The extent of Hadean contact metamorphism of sedimentary rocks, particularly of carbonate-rich sediments, must have been far less than in subsequent eons as a consequence of limited formation of carbonate platforms (Hazen and others, 2013a). Therefore, the presence and relative abundance of more than 40 skarn minerals, including åkermanite ($\text{Ca}_2\text{MgSi}_3\text{O}_7$), clintonite [$\text{CaAlMg}_2(\text{SiAl}_3)\text{O}_{10}(\text{OH})_2$], cuspidine ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$), grossular [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$], larnite (Ca_2SiO_4), lazurite [$\text{Na}_3\text{Ca}(\text{Si}_3\text{Al}_3)\text{O}_{12}\text{S}$], meionite [$(\text{Ca},\text{Na})_4(\text{Si},\text{Al})_{12}\text{O}_{24}(\text{CO}_3,\text{SO}_4,\text{Cl})$], monticellite (CaMgSiO_4), spurrite [$\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$], tilleyite [$\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$], tremolite [$\square\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$], vesuvianite [$(\text{Ca},\text{Na})_{19}(\text{Al},\text{Mg},\text{Fe})_{13}(\text{SiO}_4)_{10}(\text{Si}_2\text{O}_7)_4(\text{OH},\text{F},\text{O})_{10}$], and wollastonite (CaSiO_3), is uncertain. These species have been included in table 1 with the proviso that skarn minerals presuppose the existence of at least localized carbonate bodies. If extensive limestone deposits were lacking in the Hadean Eon, then these species would have been rare or absent. By the same token, if Mn-rich carbonates, including Mn-bearing calcite and dolomite, kutnahorite [$\text{CaMn}^{2+}(\text{CO}_3)_2$] or rhodochrosite, had not formed prior to 4 Ga, then such Mn^{2+} -silicate skarn minerals as bementite [$\text{Mn}_7\text{Si}_6\text{O}_{15}(\text{OH})_8$], bustamite ($\text{CaMn}^{2+}\text{Si}_2\text{O}_6$), caryopilite [$(\text{Mn}^{2+})_3\text{Si}_2\text{O}_5(\text{OH})_4$], johannsenite ($\text{CaMn}^{2+}\text{Si}_2\text{O}_6$), rhodonite ($\text{Mn}^{2+}\text{SiO}_3$), spessartine [$\text{Mn}^{2+}_3\text{Al}_2(\text{SiO}_4)_3$], and tephroite ($\text{Mn}^{2+}_2\text{SiO}_4$) would probably not have formed.

Impact mineralization.—The role of impact-related mineralization during the great bombardment of the Hadean Eon has been little explored. On the one hand, large bolide impacts would have continuously disrupted Earth's near-surface mineralogy, melting and/or vaporizing surface phases within a radius up to several times the diameter of the impactor. Hadean Earth may have been subjected to 20,000 impacts of meteors >1 km diameter and more than 100 impacts of objects >10 km (Glickson, 1998; Pirajno, 2009), with associated melting. Yet such events also had the potential to diversify Earth's mineralogy in at least three ways. First, impacts can produce high-pressure shock minerals such as the (nano)diamond and lonsdaleite polymorphs of carbon, the coesite and stishovite polymorphs of silica, and the wadsleyite and ringwoodite polymorphs of forsterite. These and other high-pressure phases were widely generated, both within meteorites and in the surrounding shocked country rock.

A second mineralogical consequence of impacts is their ability to excavate and disperse samples of deep crustal lithologies. Martian meteorites, which were ejected from the Martian high-crust and upper mantle, demonstrate that a fraction of such deep samples need not be subjected to extreme shock alteration, as peripheral impact zones may be ejected at high velocity (for example, Melosh, 1985; Head and others, 2002; Artemieva and Ivanov, 2004; Walton and Herd, 2007; Agee and others, 2013). Consequently, impacts must have excavated deep terrains and their associated high-pressure and high-temperature mineralogy at a time prior to plate tectonics and continental orogenesis—the primary mechanisms by which high-pressure rocks are exposed today. Thus, such regional metamorphic phases as cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), kyanite (Al_2OSiO_4), and staurolite [$\text{Fe}^{2+}_2\text{Al}_9\text{Si}_4\text{O}_{23}(\text{OH})$] may have been exposed at the surface. Note, however, that high-pressure but relatively low-temperature blueschist facies minerals, including deerite [$\text{Fe}^{2+}_6\text{Fe}^{3+}_3(\text{Si}_6\text{O}_{17})\text{O}_3(\text{OH})_5$], glaucophane [$\square\text{Na}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$], jadeite ($\text{NaAlSi}_2\text{O}_6$), and lawsonite [$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$], are associated with relatively cool and steep subduction zones—conditions that may not have occurred in the Hadean Eon and thus are excluded from table 1.

Finally, large impacts must have produced heated fracture zones that initiated regionally significant deep circumferential hydrothermal systems, possibly lasting for > 10^5 years, along crater margins (Abramov and Kring, 2005; Versh and others, 2006; Pirajno, 2009). Such large-scale fluid-rock interactions would have pre-dated modern

style subduction, arc volcanism, and associated mineralization (notably massive sulfide deposits and their associated assemblages of chalcogenide and sulfosalt minerals). Impact-triggered hydrothermal processes thus may have led to extensive hydrothermal systems, with associated local element selection, concentration, and mineralogical novelty. The dominant effect of impact hydrothermal alteration is production of clay minerals, K-feldspar, and zeolites (Allen and others, 1982; Pirajno, 2005). Of special interest, however, is the impact production of syngenetic or epigenetic metal ore deposits, as exemplified by Ni-Cu ores at the Sudbury Igneous Complex in Canada (Naldrett, 2003) and Pb-Zn-Ag-Ba mineralization at the Siljian Ring Complex in Sweden (Johansson, 1984), respectively. Similarly, large Hadean impact events may represent the earliest large-scale hydrothermal processing of crustal lithologies, and thus impact metalogenesis may predate other episodes of massive sulfide formation.

Other near-surface processes.—Additional mineral-forming processes during the Hadean Eon include vapor deposition (that is, sublimation), especially at volcanic fumaroles and shallow intrusive settings; precipitation and evaporite mineralization in marine and lacustrine aqueous environments; authigenic formation of minerals, notably in marine sediments; and freezing of water to form ice (H₂O). More than 75 mineral species (tables 1 and 2) are likely to have appeared prior to 4 Ga as a result of these relatively low-temperature, near-surface mechanisms.

A few erosion-resistant minerals must have been concentrated in detrital sediments during the Hadean Eon. The oldest known fragments of early Earth are zircon grains from the Jack Hills of Australia—some of which have cores formed at 4.4 Ga (Cavosie and others, 2005, 2007). Further examination of Archean sediments might reveal grains of more than 30 different detrital species (tables 1 and 2), including cassiterite, ilmenite, monazite, rutile, titanite, and minerals of the apatite, spinel, and tourmaline groups that might be dated to the Hadean Eon through studies of trace isotopic ratios.

In summary, observed minerals in meteorites and pre-Archean rocks, combined with analysis of known mineral-forming processes prior to 4 Ga, result in a preliminary list of 420 plausible Hadean minerals, including 221 silicates and 199 non-silicates (tables 1 and 2). The following section justifies why more than 4300 known mineral species today are excluded from this list of widespread and/or volumetrically significant Hadean Eon minerals.

POST-HADEAN MINERALS

The initial strategy in documenting possible widespread and/or volumetrically significant rock-forming and accessory Hadean Eon minerals has been to catalog species that are present in meteorites and in rocks of Eoarchean and Hadean age, and to evaluate mineral-forming processes that would have led to suites of more ephemeral phases—an approach that led to a list of 420 plausible Hadean crustal minerals. But what of the thousands of other known mineral species on Earth today? The opposite tack is to reduce the current list of more than 4800 known mineral species (as tabulated by <http://ima.ruff/info> in March, 2013) by processes of elimination.

Four criteria eliminate minerals from consideration as significant Hadean phases: (1) minerals that are exceedingly rare species today and thus were probably never widely distributed or volumetrically significant in the near-surface environment; (2) redox-sensitive minerals that require an oxygen fugacity significantly above the hematite-magnetite buffer that characterized Earth's near-surface environment prior to the Great Oxidation Event; (3) minerals that arise primarily through volcanic and orogenic processes associated with subduction and continent formation; and (4) biologically-mediated minerals, including minerals formed directly by cells through biomineralization and through biologically-assisted weathering of pre-existing minerals, as well as a variety of biologically-mediated minerals that incorporate organic molecules.

Rare Minerals

With the exception of the impact-related processes of deep excavation, shock synthesis, and associated extensive hydrothermal activity, no significant mineral-forming processes in the Hadean Eon have been identified that are not widely in play today. Therefore, if a mineral species is exceedingly rare on Earth today, the probability is great that it was not a widespread or volumetrically significant mineral during Earth's first 550 million years. Two criteria are proposed to define a mineral as rare, and thus exclude it from further consideration: (1) the mineral is documented from fewer than 11 "localities" worldwide (as tabulated in the locality field of <http://mindat.org>, though note that some "localities" represent mineral districts with multiple surface expressions), and (2) the mineral occurs in isolated masses less than 1 centimeter in maximum dimension (as documented by specimen descriptions and photographs on the mindat.org website).

By these criteria, most of the more than 4800 IMA approved mineral species are rare. A survey of the number of documented localities for all species (<http://mindat.org>) reveals that more than 66 percent of all mineral species are known from 10 or fewer localities, more than 50 percent of species are known from 5 or fewer localities, and more than 25 percent of all known mineral species are recorded from only one locality worldwide. By contrast, only ~1200 minerals (approximately 25% of known species) are sufficiently common to be documented from more than 25 worldwide localities. With the possible exception of a few uncommon meteorite minerals (for example, the phosphide schreibersite), it seems likely that those minerals that are extremely rare on Earth today would not be widespread or volumetrically significant on the Hadean Earth and thus can be excluded from additional consideration.

A caveat is in order with respect to documented mineral localities. In some cases, rare minerals may be disproportionately reported because they incorporate economically important elements or because they are brightly colored and thus easily identified. For example, in a tabulation of all mineral species listed in order of the number of reported worldwide localities on mindat.org (<http://mindat.org>), gold (Au) ranks third with more than 22,300 entries, behind only quartz and pyrite (FeS_2). By contrast, the abundant but less visually striking or valuable alkali feldspar minerals albite, microcline (KAlSi_3O_8), and orthoclase (also KAlSi_3O_8) rank 15th, 40th, and 74th in terms of number of reported localities, respectively. Other common rock-forming minerals, including forsterite (164th), enstatite (199th), and anorthite (300th), underscore the biases inherent in this measure of relative rarity. Nevertheless, any mineral that is recorded from fewer than 11 localities worldwide today is unlikely to have been a widespread or volumetrically significant phase during the Hadean Eon. This criterion, alone, eliminates two-thirds of known mineral species from further consideration in the preliminary list of Hadean Eon minerals.

This approach—elimination of rare minerals from a list of plausible Hadean Eon species—is bolstered by evidence from systematic examinations of the mineral evolution of several rare elements. The official IMA list of minerals records 72 different essential chemical elements (table 3)—that is, elements that are integral to the definition of one or more mineral species (as defined at [http://ima.ruff/info](http://ima.ruff.info)). However, a significant number of those elements occur in trace amounts—less than a few parts per million in Earth's crust (table 3). Thus, these elements require extensive selection and concentration to produce their own minerals (as opposed to occurring as trace or minor substituting elements in other minerals—compositional effects that are critical to understanding the geochemistry of many rare elements, but do not warrant the naming of a new mineral species). Studies of several of these elements, including Be (Grew and Hazen, 2009); B (Grew and Hazen, 2010b; Grew and others,

TABLE 3

The 72 essential mineral-forming chemical elements, with average crustal abundance (ACA in ppm; Emsley, 1991), the number of approved mineral species [approved species compiled from the official mineral list of the International Mineralogical Association as of September 2012 ([http://ima.ruff/info](http://ima.ruff.info))], the estimated number of Hadean Eon species (see text), and percentage of total species that may have appeared in the Hadean Eon. Elements denoted (X) are not expected to produce any Hadean Eon minerals for a variety of geochemical and/or crystal chemical reasons

Element	ACA	# IMA Species	# Hadean Species	Percent in the Hadean Eon
H	1520	2658	202	7.6
Li (X)	20	113	0	0
Be (X)	2.6	110	0	0
B	10	251	2	0.8
C	480	387	37	9.6
N (X)	25	86	0	0
O	474000	3792	347	9.2
F	950	351	17	4.8
Na	23000	893	87	9.7
Mg	23000	597	103	17.3
Al	82000	963	157	15.8
Si	277000	1391	227	16.3
P	1000	548	15	2.7
S	260	955	68	7.1
Cl	130	334	11	3.3
K	21000	423	34	8.0
Ca	41000	1146	133	11.6
Sc (X)	16	16	0	0
Ti	5600	325	20	6.2
V (X)	160	190	0	0
Cr	100	90	8	8.9
Mn	950	498	40	8.0
Fe	41000	1020	106	10.4
Co	20	59	1	1.7
Ni	80	141	23	16.3
Cu	50	603	13	2.1
Zn	75	229	10	4.4
Ga (X)	18	5	0	0
Ge (X)	1.8	27	0	0
As	1.5	536	13	2.4
Se (X)	0.05	112	0	0
Br (X)	0.37	12	0	0
Rb (X)	90	3	0	0
Sr	370	121	3	2.5
Y	30	116	1	0.8
Zr	190	118	4	3.4
Nb (X)	20	133	0	0
Mo	1.5	54	1	1.9
Ru (X)	0.001	8	0	0
Rh (X)	2×10^{-4}	14	0	0
Pd (X)	6×10^{-4}	61	0	0
Ag	0.07	158	2	1.2
Cd (X)	0.11	68	0	0
In (X)	0.049	11	0	0
Sn	2.2	92	1	1.1
Sb (X)	0.2	225	0	0
Te (X)	0.005	151	0	0
I (X)	0.14	24	0	0
Cs (X)	3	17	0	0
Ba	500	216	4	1.9
La	32	45	1	2.2

TABLE 3
(continued)

Element	ACA	# IMA Species	# Hadean Species	Percent in the Hadean Eon
Ce	68	147	2	1.4
Nd	38	26	1	3.8
Sm (X)	7.9	2	0	0
Gd (X)	7.7	1	0	0
Dy (X)	6	1	0	0
Er (X)	3.8	1	0	0
Yb (X)	5.3	5	0	0
Hf (X)	3.3	1	0	0
Ta (X)	2	57	0	0
W (X)	1	39	0	0
Re (X)	4 x 10 ⁻⁴	2	0	0
Os (X)	1 x 10 ⁻⁴	6	0	0
Ir (X)	3 x 10 ⁻⁶	17	0	0
Pt	0.001	31	1	3.2
Au	0.0011	30	1	3.3
Hg	0.05	90	1	1.1
Tl (X)	0.6	48	0	0
Pb	14	470	2	0.4
Bi (X)	0.048	203	0	0
Th	12	32	3	9.4
U	2.4	232	1	0.4

2011); Hg, Br, and I (Hazen and others, 2012); and Mo (McMillan and others, 2010; Golden and others, 2013), suggest that it took hundreds of millions, if not billions, of years of fluid-rock interactions in the crust and upper mantle to concentrate these elements sufficiently to form their own separate minerals. For example, no beryllium minerals have been reported from meteorites and the oldest known occurrences are beryl and phenakite from an “albitite pegmatoid” in the 2,969 ± 17 Ma Gravelotte emerald deposit of the Murchison greenstone belt, South Africa (Robb and Robb, 1986; Grundmann and Morteani, 1989; Poujol, 2001). Similarly, boron minerals are unknown from meteorites and the oldest reported occurrences are metamorphic tourmaline group minerals, notably dravite [NaMg₃Al₆(Si₆O₁₈)(BO₃)₃(OH)₃OH] and schorl [NaFe²⁺₃Al₆(Si₆O₁₈)(BO₃)₃(OH)₃OH], from the ~3.65 Ga Isua Complex, Greenland (Meng and Dymek, 1987; Meng, ms, 1988). In the case of Hg, there are reports of trace micro- or nanoscale HgS (polymorph unknown) in a few meteorites (Lauretta and others, 2001; Caillet Komorowski and others, 2009, 2010), but no significant terrestrial Hg mineralization is preserved in rocks older than about 3.1 Ga (Hazen and others, 2012), nor are there any known Precambrian occurrences of I or Br minerals [though iodargyrite (AgI) and bromargyrite (AgBr) are found as Cenozoic secondary alteration minerals at the Mesoproterozoic deposits of Broken Hill, Australia].

In this regard it is important to reiterate that an increasing number of new minerals, particularly in meteorites and other extraterrestrial samples, has been identified using microbeam instruments as isolated nano-phase constituents. While such nano-materials, particularly those in meteorites, must have been present in the Hadean Eon, such rare and volumetrically minor phases are not included in the inventory of widely distributed rock-forming and accessory Hadean minerals.

Based on these studies, minerals of at least 33 of the 72 essential chemical elements may not have occurred to any significant degree prior to 3.5 Ga, and thus have been eliminated from consideration in developing a list of Hadean minerals,

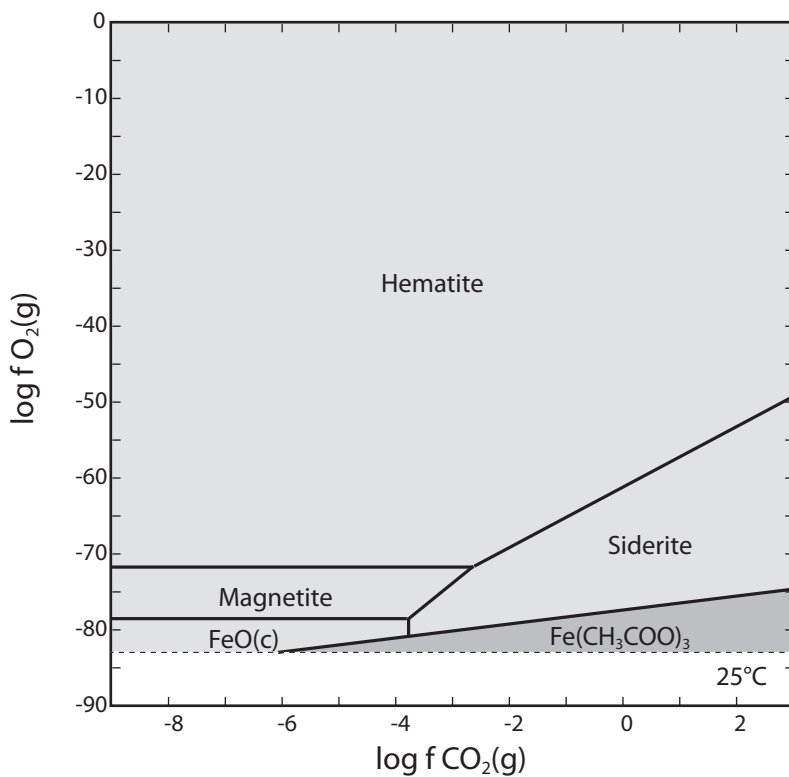


Fig. 1. The stabilities of iron oxides and carbonates as a function of f_{O_2} and f_{CO_2} , based on thermodynamic data for aqueous species (Shock and others, 1997) and minerals (Helgeson and others, 1978). Note that the oxygen fugacity of a near-surface terrestrial or marine environment enriched in ferrous iron is effectively buffered by hematite plus magnetite ($\log f_{\text{O}_2} \sim -72$ at standard temperature and pressure). At these conditions, precipitation of ferrous iron carbonate requires $\log f_{\text{O}_2} < -68$ at STP, assuming $\log f_{\text{CO}_2} < -2$. Note that the lower dashed line in the diagram at $\log f_{\text{O}_2} = -83.1$ represents the lower stability of water at 1 atm H₂. The diagram, courtesy of Dimitri Sverjensky, was calculated with Geochemists Workbench (Bethke 1996).

while 14 other rare elements are likely to have been represented by only one or two species (see table 3). Thus, the only likely Hadean minerals of B are the dravite-schorl series of the tourmaline group (Grew and Hazen, 2010b; Grew and others, 2011). Similarly, the only likely Hadean mercury and molybdenum minerals are the sulfides cinnabar (HgS) and molybdenite (MoS₂), respectively, while uranium and thorium mineralization may have been restricted to the oxides uraninite (UO₂) and thorianite (ThO₂), and the orthosilicate thorite (ThSiO₄).

Redox-Sensitive Elements and their Minerals

The presumed anoxia of the Hadean Eon severely restricts the diversity of thermodynamically stable mineral species. Numerous lines of evidence have been cited to establish Earth's relatively low oxygen fugacity prior to 3 Ga (see Hazen and others, 2008, 2009, 2013a; Sverjensky and Lee, 2010; and references therein). The oxygen fugacity of Earth's shallow (>1 cm deep) sub-surface marine and terrestrial environments prior to 4 Ga is thus postulated to have been close to that of the hematite-magnetite buffer [$\log f_{\text{O}_2} \sim -72$ at standard temperature and pressure (STP); fig. 1], based on the widespread availability of soluble Fe²⁺ in the oceans and paleosols. Photo-dissociation of water in the upper atmosphere and other photo-

oxidation reactions at the surface may have led to localized surface environments of higher oxidation fugacity, but shallow subsurface (that is, ≥ 1 cm) and aqueous environments (where almost all mineralization occurred) were effectively buffered at redox conditions more than 70 log units lower than those of extensive volumes of the oxidized shallow subsurface today. This environmental redox constraint places severe limits on the thermodynamically stable mineralogy of the Hadean Eon (Sverjensky and others, 2010).

Copper provides a dramatic example of the redox-controlled mineralogical parsimony of the Hadean Eon. Though relatively scarce at ~ 50 ppm average crustal abundance, copper today is represented by more than 600 IMA-approved species (table 3). Yet by the redox criteria noted above, no more than 13 copper minerals could have been widely distributed in the Hadean Eon. These minerals, including native copper (Cu), chalcocite (Cu_2S), chalcopyrite (CuFeS_2), covellite (CuS), cubanite (CuFe_2S_3), and 8 other sulfides and sulfosalts, may be the only plausible copper minerals prior to significant near-surface oxidation (table 2). Significantly, no copper oxides, silicates, carbonates, sulfates, arsenates, or phosphates—minerals that account for 370 of the known copper species—are included. The great majority of these excluded minerals represent secondary minerals that form through near-surface oxidation of copper sulfides and their alteration products.

A key assumption of this study is that Earth's near-surface redox environment during the Hadean Eon was constrained to lie near or below the hematite-magnetite buffer by the presence of ferrous iron in both oceans and sediments: STP, $\log f_{\text{O}_2}$ was thus close to -72 (Garrels and Christ, 1965; fig. 1). By contrast, the native copper (Cu^0)-cuprite (Cu^{1+}_2O) buffer at STP is $\log f_{\text{O}_2} = -52$, or 20 log units above the average value of the Hadean surface environment (fig. 2). Consequently, cuprite and other Cu^{1+} phases with Cu^{1+} -O are unlikely to have formed. The cuprite-tenorite (Cu^{2+}O) buffer, at $\log f_{\text{O}_2} = -38$, is 14 log units higher than native copper-cuprite (fig. 2). Therefore, hundreds of mineral phases with Cu^{2+} -O bonds—representing most copper minerals, including many brilliant blue and green phases—are even less likely than Cu^{1+} phases to have formed in the Hadean Eon. By contrast, the formation of Cu-S bonds in chalcocite (Cu_2S) and covellite (CuS) is dependent primarily on f_{S_2} ; at $\log f_{\text{S}_2} > -44$ these copper sulfide phases will form at any oxygen fugacity below 10^{-52} provided the sulfur fugacity is sufficiently high (Garrels and Christ, 1965), and thus must be included in an inventory of potential Hadean minerals.

Similar arguments can be applied to the minerals of numerous other redox-sensitive elements. For example, uranium, with an average crustal abundance < 3 ppm, is known as an essential element in 232 minerals (table 3), yet Hazen and others (2009) concluded that fewer than 20 U mineral species would have been present prior to ~ 2.4 Ga and the Great Oxidation Event as a consequence of redox limitations. Based on that constraint, coupled with the scarcity of uranium and the time it must have taken to concentrate U into mineral-forming solutions, uraninite (UO_2) is the only probable Hadean uranium mineral, though an argument might be made for the inclusion of the common U^{4+} silicate coffinite $\{\text{U}[\text{SiO}_4(\text{OH})_4]\}$, as well. In particular, at neutral pH and STP U^{6+} (uranyl) species are not stable at $\log f_{\text{O}_2} < -50$. More than 210 of the known uranium minerals incorporate U^{6+} , and are unlikely to have occurred during the Hadean Eon (Hazen and others, 2009).

A significant exception to the geochemical limitations on the Hadean occurrence of U^{6+} ions is the production of uranyl ions by the phenomenon of auto-oxidation, which occurs in uraninite as a consequence of the radiometric decay of a U^{4+} ion to Pb^{2+} and the associated local oxidation of another U^{4+} ion to U^{6+} within the uraninite crystal lattice. Given sufficient time, as much as 20 percent of uranium in a uraninite crystal can thus be oxidized and lead to localized development of uranyl minerals,

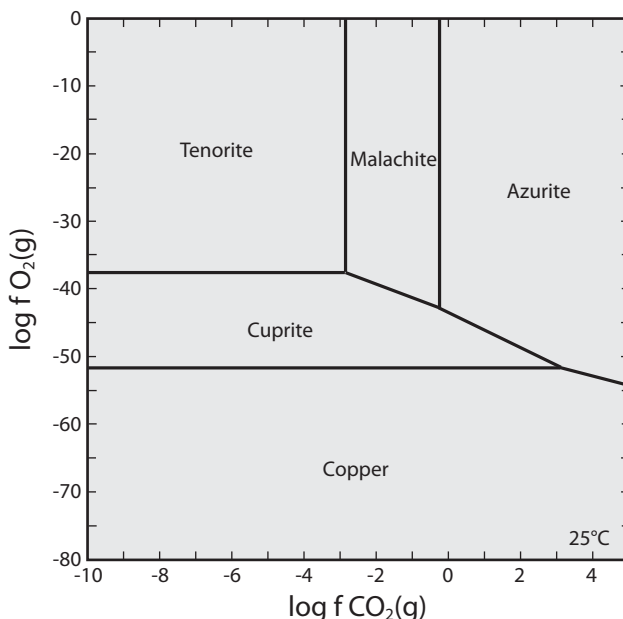


Fig. 2. The stabilities of the copper oxides and carbonates as a function of f_{O_2} and f_{CO_2} , based on thermodynamic data for aqueous species (Shock and others, 1997), Cu carbonate minerals (Preis and Gamsjäger, 2002), and Cu oxide minerals (Helgeson and others, 1978). If the oxygen fugacity of a near-surface terrestrial or marine environment enriched in ferrous iron is effectively buffered by hematite plus magnetite ($\log f_{\text{O}_2} \sim -72$ at standard temperature and pressure; see fig. 1), then native copper is the only stable copper-bearing phase in the Cu-C-O-H system. By contrast, the common copper carbonates azurite and malachite require $\log f_{\text{O}_2} > -43$ at STP, assuming $\log f_{\text{CO}_2} < -2$, which precludes their formation prior to the Great Oxidation Event. Thermodynamic data used to construct this diagram came from aqueous species (Shock and others, 1997). The diagram, courtesy of Dimitri Sverjensky, was calculated with Geochemists Workbench (Bethke, 1996).

notably the mixed-valence mineral ianthinite [$\text{U}^{4+}_2(\text{U}^{6+}\text{O}_2)_4\text{O}_6 \cdot 9\text{H}_2\text{O}$], as well as schoepite [$(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$] and becquerelite [$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$] (Finch and Ewing, 1992; Finch, ms, 1994; Finch and Murakami, 1999). However, given the 4.46 Ga half-life of ^{238}U and the likelihood that it took several hundred million years to concentrate crustal U sufficiently to form uraninite, auto-oxidation is unlikely to have had a significant influence on Hadean uranium mineralogy.

Lead, in spite of its low crustal abundance (14 ppm), is represented by 470 mineral species. As with uranium, lead mineralization is severely restricted under anoxic conditions. The Pb-PbO buffer at STP is $\log f_{\text{O}_2} \sim -65$. Garrels and Christ (1965) calculate that galena (PbS) is stable at the presumed Hadean $\log f_{\text{O}_2} \sim -72$ and $\log P_{\text{SO}_2} > -22$. Note, however, that the common lead sulfate anglesite (PbSO_4) is not stable under these reducing conditions. Furthermore, more than 200 other lead oxides, hydroxides, sulfates, carbonates, phosphates, arsenates, vanadates, and selenates, including beaudantite [$\text{PbFe}^{3+}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$], cerussite (PbCO_3), dundasite [$\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$], hildalگوite [$\text{PbAl}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})$], hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$], lanarkite [$\text{Pb}_2\text{O}(\text{SO}_4)$], leadhillite and macphersonite [both $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$], paulmooreite ($\text{Pb}_2\text{As}^{3+}_2\text{O}_5$), pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$], and susannite [$\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$], are known today almost exclusively in the oxidized zones of lead deposits (Anthony and others, 2000). Therefore, it seems likely that none of these numerous lead minerals would have been present in the Hadean

Eon (though thermochemical calculations of the redox limitations on lead mineralization would be welcome).

Manganese is a relatively abundant crustal element (980 ppm) that is essential in approximately 500 mineral species. However, most of those minerals are also precluded from the Hadean inventory as a consequence of redox considerations. Today, manganese minerals incorporate Mn^{2+} as in manganosite (MnO), Mn^{3+} as in manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and Mn^{4+} as in pyrolusite (MnO_2). However, the $\text{MnO-Mn}_2\text{O}_3$ buffer lies at $\log f_{\text{O}_2} \sim -67$, which is several log units above the hematite-magnetite buffer (Garrels and Christ, 1965). Therefore, oxides and silicates with Mn^{3+} may be inhibited, though tables 1 and 2 tentatively include several Mn^{3+} minerals, including bixbyite ($\text{Mn}^{3+}_2\text{O}_3$), braunite ($\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$), groutite [$\text{Mn}^{3+}\text{O}(\text{OH})$], hetaerolite, hausmanite ($\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$), manganite, and piemontite [$\text{Ca}_2\text{Mn}^{3+}\text{Al}_2(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$]. However, the $\text{Mn}_2\text{O}_3\text{-MnO}_2$ buffer lies at $\log f_{\text{O}_2} \sim -14$, so Mn^{4+} minerals are excluded from consideration as possible Hadean phases.

Another important example of a redox-sensitive chemical system is provided by the minerals of the relatively rare element arsenic (average crustal abundance ~ 1.5 ppm). Arsenic is chemically versatile with four natural oxidation states— As^{3-} , As^0 , As^{3+} , and As^{5+} —and is represented today by more than 530 different mineral species (table 3). Oremland and others (2009) have suggested that arsenic was more abundant at Earth's surface prior to 4 Ga than it is today, because of the input of P-rich meteorites (which are correspondingly enriched in As), as well as by volcanic distillation of volatile arsenic. Nevertheless, hundreds of documented arsenite (As^{3+}) and arsenate (As^{5+}) minerals are known almost exclusively as secondary minerals in oxidized ore zones (Anthony and others, 2000), so arsenite minerals are excluded from the list. Accordingly, only 13 arsenic minerals (table 2) are cited as possible Hadean Eon phases, and it is possible that only arsenopyrite (FeAsS), native arsenic (As), orpiment (As_2S_3), and realgar (AsS)—the four most abundant arsenic minerals today—were present prior to 4 Ga. Table 2 also tabulates the most common arsenides and sulfosalts of Cu, Fe, and Ni, including enargite (Cu_3AsS_4), gersdorffite (NiAsS), löllingite (FeAs_2), maucherite ($\text{Ni}_{11}\text{As}_8$), nickeline (NiAs), nickelskutterudite (NiAs_2), pararammelsbergite (NiAs_2), rammelsbergite (NiAs_2), and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$). Pararealgar (AsS), which is known today exclusively via the photolysis of realgar, is not included, nor are any of the hundreds of arsenate or arsenite minerals. However, the mineral evolution of arsenic remains a rich and unexplored subject for further study.

Zinc, with 229 recognized species, is yet another element whose mineral diversity is redox-sensitive and thus deserves more study. Pending analysis of their thermochemical stability, several common zinc minerals have been included as possible Hadean species, including native zinc (Zn); the sulfides sphalerite and wurtzite (both ZnS); the spinels franklinite ($\text{ZnFe}^{3+}_2\text{O}_4$), gahnite (ZnAlO_4), and hetaerolite ($\text{ZnMn}^{3+}_2\text{O}_4$); the orthosilicate willemite (Zn_2SiO_4); the clay minerals fraipontite [$(\text{Zn,Al})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4$] and sauconite [$\text{Na}_{0.3}\text{Zn}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$]; and the oxide zincite (ZnO). However, many common zinc minerals today, including the carbonates aurichalcite [$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$], brianyoungite [$\text{Zn}_3\text{CO}_3(\text{OH})_4$], hydrozincite [$\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$], and smithsonite (ZnCO_3), are known only as secondary minerals formed in the oxidized zones of zinc-bearing deposits and thus may not have been present in the Hadean Eon. Therefore, it is possible that willemite would also have been unlikely to form as a skarn mineral, though willemite is included in table 1 as a possible regional metamorphic phase (Johnson and Skinner, 2003). Similarly, the sulfates bianchite ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$), boyleite ($\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$), goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), and gunningite ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$); the arsenates adamite [$\text{Zn}_2\text{AsO}_4(\text{OH})$], arsenohopeite [$\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$], köttigite [$\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$], and legrandite [$\text{Zn}_2\text{AsO}_4(\text{OH}) \cdot \text{H}_2\text{O}$]; and the phosphates hopeite and parahopeite [both $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$], phosphophyllite

[$\text{Zn}_2\text{Fe}^{2+}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$], and schlozite [$\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$]; and more than 150 other zinc minerals are known only from the oxidized zones of secondary mineralization of zinc ore bodies. Consequently, while further work on the stability of zinc minerals under varying f_{O_2} - f_{S_2} - f_{CO_2} conditions is warranted, the great majority of zinc minerals have been excluded from the list of plausible Hadean mineral phases.

Similar analyses might be applied to the minerals of several other mineral-forming elements, including Ag, Co, Cr, Mo, Ni, Sb, Se, V, and W, most of whose known mineral species would not have played any significant role in the paleomineralogy of the Hadean Eon. In summary, analyses of thermodynamic limitations of redox-sensitive minerals during the Hadean Eon suggest that more than half of all known mineral species could not form in a near-surface environment buffered at $\log f_{\text{O}_2} = -72$.

Minerals Associated with Plate Tectonics

A significant difference between the Hadean Eon and today is the nature and extent of plate tectonics. Several lines of evidence, including the nature of Paleoproterozoic terranes, geodynamic models, and mineral inclusions in diamonds (Shirey and Richardson, 2011; Dhuime and others, 2012; Shirey and others, 2013), have been invoked to suggest that modern-style plate tectonics was not established globally until ~ 3 Ga. Prior to that time a significant component of orogenesis may have been a consequence of vertical tectonics associated with mantle plumes (Van Kranendonk, 2011, 2012), perhaps further disrupted by major impact events. Thus, the Hadean Eon may not have experienced the formation of significant deeply-rooted continental landmasses, subduction of wet crustal material, arc volcanism, and associated fluid-rock interactions and reworking of the overlying upper mantle and crust.

A number of near-surface minerals occur today primarily as a consequence of volcanogenic and orogenic processes associated with convergent plate boundaries. For example, massive sulfide and porphyry copper deposits commonly arise from hydrothermal fluids associated with volcanism above subducting lithosphere. These deposits are known to host numerous rare accessory minerals, including hundreds of sulfosalts, hydroxyl sulfides, sulfates, arsenates, and other alteration products that may not have occurred prior to the extensive fluid-rock interactions and element concentration associated with these processes. In addition, the subduction, high-pressure alteration, and buoyant uplift of crustal wedges results in the surface exposure of blueschist facies rocks with their distinctive suites of high-pressure (though relatively low-temperature) minerals—phases that might not otherwise appear in shallow crustal environments. An important caveat regarding deep crustal phases is that some deeply buried lithologies may have been excavated by asteroid impacts, which represent a mode of mineralization that was far more significant during the Hadean Eon than at any subsequent interval.

Another consequence of plate tectonics is the development of extensive landmasses, stranded seas, and associated complex suites of evaporite minerals. Of the more than 400 known evaporitic chloride, fluoride, borate, carbonate, and sulfate minerals, only two-dozen of the most common, thermodynamically stable phases are included in table 2, based on the assumption that such evaporite bodies would have been far less extensive or evolved prior to the formation of large continents. However, if extensive subareal continental landmasses were well established in the Hadean Eon, then correspondingly diverse evaporite deposits may have been present.

Also excluded are most of the ~ 500 rare minerals, including a host of phosphate minerals, associated with complex pegmatites. The most mineral-rich complex pegmatites are associated with peraluminous S-type granites, which require continent formation, development of Al-rich sedimentary sequences, and subduction and partial melting of these sediments (Chappell and White, 2001; London 2008).

Biologically-Mediated Minerals

Biological processes have affected Earth's near-surface mineralogy in at least four significant ways since the prebiotic Hadean Eon. Biomineralization, notably the precipitation of extensive carbonate platforms and other carbonate-rich sediments, is one obvious mineralogical consequence of biology. More than 50 biominerals—crystalline phases precipitated by living organisms—have been catalogued (see table 3 in Hazen and others, 2008). However, with the possible exceptions of the rare phosphate hazenite [$\text{KNaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$], minerals formed by life also occur by wholly inorganic processes. However, biomineralization has dramatically altered the near-surface distribution and morphologies of carbonates (Hazen and others, 2013a), phosphates (Burnett and Riggs, 1990; Hazen and others, 2008), and other minerals.

Near-surface oxidation is a second important consequence of biology (see above). Most mineral species arise as a consequence of near-surface oxidation and weathering of pre-existing minerals following the Great Oxidation Event, which occurred approximately 2.4 to 2.2 billion years ago following the rise of cyanobacteria (Holland, 1984, 2002). Consequently, numerous redox-sensitive minerals of As, Co, Cu, Fe, Mn, Ni, S, U, and Zn, and many other elements, would not have occurred prior to 2.4 Ga when oxygenic photosynthesis produced an atmosphere with >1 percent present levels of atmospheric oxygen.

A third mineralogical consequence of biology is the development of soils and associated clay mineralization following the rise of the terrestrial biosphere (Hazen and others, 2013b). The actions of plant roots, assisted by the rise of mycorrhizal fungi, have become a principal agent of terrestrial weathering during the Phanerozoic Eon (Weed and others, 1969; Silverman and Munoz, 1970; Bonneville and others, 2009; Hazen and others, 2013b).

Finally, life has led indirectly to more than 50 organic minerals, including organic molecular crystals and minerals with organic molecular anions (Hazen and others, 2013a), most of which form in cave guano deposits, in decayed vegetation, or in coal. Organic molecular minerals are represented, for example, by at least 20 Van der Waals-bonded crystals that are found primarily in coal deposits. Examples include hydrocarbon minerals [for example, kratochvilite ($\text{C}_{13}\text{H}_{10}$), fichtelite ($\text{C}_{19}\text{H}_{34}$), dinite ($\text{C}_{20}\text{H}_{36}$), and evenkite ($\text{C}_{24}\text{H}_{48}$)]; the purine guanine ($\text{C}_5\text{H}_5\text{N}_5\text{O}$); and the nickel porphyrin mineral abelsonite [$\text{Ni}(\text{C}_{31}\text{H}_{32}\text{N}_4)$]. Approximately two-dozen minerals incorporate varied organic anions that are bonded to Ca, Cu, Mg, Na, and other metal cations. A dozen oxalate minerals with the $(\text{C}_2\text{O}_4)^{2-}$ anion are especially significant among these organic salts. Weddellite [$\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$] is by far the most common of these phases, with reports from such varied environments as bat guano, sediments derived from lichens, human kidney stones, the saguaro cactus (*Carnegiea gigantea*), and the depths of the Weddell Sea. Other organic minerals incorporate formate ions $(\text{HCOO})^{-1}$, for example in formicate [$\text{Ca}(\text{CHOO})_2$]; acetyl ions $(\text{CH}_3\text{COO})^{-1}$ in calclacite [$\text{Ca}(\text{CH}_3\text{COO})\text{Cl} \cdot 5\text{H}_2\text{O}$]; methyl sulfonate ions $(\text{CH}_3\text{SO}_3)^{-1}$ in ernstburkite [$\text{Mg}(\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$]; and thiocyanate ions $(\text{SCN})^{-1}$ in julienite [$\text{Na}_2\text{Co}(\text{SCN})_4 \cdot 8\text{H}_2\text{O}$]. None of these minerals is likely to have been a widespread phase prior to the Phanerozoic Eon, though some carbonaceous chondrite meteorites contain significant stores of small organic molecules, which might have concentrated locally into organic crystals. Indeed, it is possible that prebiotic crystals of amino acids or polycyclic aromatic hydrocarbons might represent mineral species that arose exclusively in the prebiotic Hadean environment.

MINERALS AND THE ORIGIN OF LIFE

A recurrent theme in research on the origins of life is the probable diverse roles of mineral surfaces in protecting, selecting, concentrating, templating, and catalyzing

reactions of prebiotic organic molecules. Bernal (1951) and Goldschmidt (1952) independently speculated on the possible influences of a variety of minerals in the origins of life, and dozens of subsequent authors have outlined both general principles and detailed scenarios for mineral-mediated biogenesis (for reviews, see Lahav, 1994, 1999; Orgel, 1998; Hazen, 2005, 2006).

Among the diverse mineral groups that have been considered in origins research, clay minerals are most frequently cited (Cairns-Smith, 1977, 1982, 2005; Lahav and others, 1978; Cairns-Smith and Hartmann, 1986; Ferris and Ertem, 1992, 1993; Ferris, 1993, 2005; Heinen and Lauwers, 1996; Ertem and Ferris, 1996, 1997; Hanczyc and others, 2003). Sulfides of transition metals, including Co, Cu, Fe, and Ni, have been investigated for their potential to catalyze biosynthetic reactions (Wächtershäuser, 1988a, 1988b, 1990a, 1990b, 1993; Blöchl and others, 1992; Russell and others, 1994; Russell and Hall, 1997; Huber and Wächtershäuser, 1997, 1998; Brandes and others, 1998; Cody and others, 2000, 2001, 2004; Huber and others, 2003, 2012; Cody, 2004, 2005). Among the many other common rock-forming minerals that have been considered are quartz (Bonner and others, 1974, 1975; Soai and others, 1999; Evgenii and Wolfram, 2000), feldspars (Parsons and others, 1998; Smith, 1998), zeolites (Smith, 1998; Smith and others, 1999), olivines (Berndt and others, 1996; McCollom and Seewald, 2001), rutile (Summers and Chang, 1990; Jonsson and others, 2009), hydroxides (Holm and others, 1993; Weber, 1995; Pitsch and others, 1995), hydroxyl-apatite (Weber, 1982; Acevedo and Orgel, 1986; Benner and Hutter, 2002), and carbonates (Hazen and others, 2001). In addition, less common minerals such as ferrous metals alloys (Smirnov and others, 2008), phosphides (Pasek and others, 2007), and borates (Ricardo and others, 2004; Grew and others, 2011) have also been considered in origin scenarios.

Of these varied mineral species invoked in the origins of life, most are likely to have been present during the Hadean Eon. However, Grew and others (2011) have questioned whether borates are plausible prebiotic minerals and have called for an increased focus on Earth's early boron cycle to resolve this issue.

UNANSWERED QUESTIONS IN HADEAN MINERALOGY

The preceding analysis suggests that the Hadean Eon hosted no more than ~420 minerals that were widespread and/or volumetrically significant. However, several questions central to this topic remain unresolved and thus represent opportunities for future research.

What Preservation Biases Affect the Early Rock Record?

Anhaeusser (1981) noted that the absence of extensive Archean ore deposits might be a consequence of the recycling of minerals during “the initial turbulent episode of protocontinent development,” by destruction caused by subsequent tectonic events, or because “mineralizing events or conditions may not have evolved sufficiently for metal concentrations to have formed in significant amounts.” Meyer (1985) echoed this latter viewpoint, noting: “In a few cases, the concentration process may involve only a few major steps, such as settling of early-formed chromite crystals in an ultrabasic . . . magma, but generally ores are the products of much more complicated systems of rock-forming events taking place over substantial intervals of geologic time.” It is not yet possible to identify the relative importance of primitive mineralization processes (implying a parsimonious mineral diversity) versus biases imposed by differential erosion of a more mineralogically varied Hadean landscape. An important pursuit in this regard is continued scrutiny of Archean sandstones for earlier detrital grains of U-bearing phases other than zircons—U-bearing apatite, monazite, or tourmaline, for example—that might yield ages of formation and thus shed light on the mineralogical character of the Hadean crust. Additionally, isotopic analyses of

these detrital grains might point to modes of formation; for example, boron isotopes of ancient tourmaline grains might reveal processing through evaporite borates, which in turn would suggest early establishment of significant continental landmasses with inland seas.

What Mineralogical Consequences Arise From Giant Impacts?

Frequent impacts of objects greater than 1 kilometer in diameter represent an important difference between the Hadean Eon and subsequent geological periods—one that may have had mineralogical consequences (see above). An important unresolved question is in regard to the nature and extent of deep, long-lived hydrothermal systems that may have been established in the circumferential fracture zones of such impact sites (Abramov and Kring, 2005; Versh and others, 2006; Pirajno, 2009). At a time prior to modern-style subduction, these deep hydrothermal zones may have played a significant role in selecting, concentrating, and transporting rare elements into mineralized zones of significant diversity, possibly including Earth's earliest metal-rich ore bodies.

What Are the Mineralogical Consequences of an Anoxic Near-Surface Environment?

Hazen and others (2008) suggested that as many as two-thirds of known mineral species could not have formed in the presumed anoxic Hadean environment. Two lines of research could amplify, or add nuance, to this contention. First, the widespread occurrence of ferrous iron in both Hadean oceans and paleosols would have effectively buffered oxygen fugacity at $\sim 10^{-72}$ (at STP) prior to 4 Ga. However, it is unresolved as to the extent to which local environments might have deviated from this value, for example through upper atmosphere water dissociation and hydrogen escape, photo-oxidation, ionizing effects of lightning, volcanic exhalations, and impacts. Modeling of these early Earth processes could point to a wider range of near-surface oxygen fugacity.

In addition, further thermochemical modeling of mineral-forming reactions for a variety of redox-sensitive elements is warranted. Garrels and Christ (1965) present analyses for some Cu, Fe, Mn, and Ni minerals, but further studies on those transition elements, as well as other cations (for example, Ag, Co, Cr, Hg, Mo, Pb, Sn, V, W, and Zn) and anionic species (notably $\text{As}^{3+}\text{O}_3^{3-}$, $\text{As}^{5+}\text{O}_4^{3-}$, CO_3^{2-} , PO_4^{3-} , and SO_4^{2-}), is warranted.

When Did Plate Tectonics Start?

Hazen and others (2008) have suggested that modern-style subduction played a potentially significant role in the mineralogical diversification of early Earth, for example through new modes of volcanism; emplacement of massive sulfide and other hydrothermal ore deposits; collisional orogenies and associated hydrothermal mineralization; the exposure of deeply-subducted wedges, which host suites of high-pressure minerals; and the establishment of extensive landmasses with associated inland evaporites and marginal sedimentary sequences. Debates continue regarding the timing of the transition from an early period of vertical plume-driven tectonics to modern-style lateral tectonics (Condie, 1989; Foley and others, 2003; Furnes and others, 2007; Condie and Pease, 2008; Pease and others, 2008; Van Kranendonk, 2011, 2012; Dhuime and others, 2012; Cawood and others, 2013)—a question that has profound implications for Hadean mineral diversity.

In this regard, the formation of continents represents an especially important consideration for Earth's early mineral evolution. For example, extensive landmasses are a prerequisite for the sedimentary wedges that lead to S-type granites, which in turn are a prerequisite for many complex pegmatites—a significant source of mineralogical diversity (for example, London, 2008). Note that complex pegmatites enriched in Li,

Cs, and Ta appear to arise primarily from S-type granites, which represent the burial of aluminous sediments, metamorphism (to schists and aluminous gneisses), and partial melting of these metasediments (Chappell and White, 2001; Černý and Ercit, 2005; Bradley, 2011). S-type granites are often associated with continental assembly, including subduction-related accretion of terranes and consequent orogenesis and crustal thickening (Martin and De Vito, 2005; Tkachev, 2011). By contrast, pegmatites enriched in Nb, Y, and F are thought to be derived from A-type (anorogenic) granites formed by partial melting of deep crustal lithologies, including basalt and gneissic granulites (Eby, 1990). Further study of the temporal distribution and mineralogy of complex pegmatites might thus reveal aspects of the nature and timing of crustal tectonic processes.

If the onset of plate tectonics was delayed until significantly after 4 Ga, then it follows that there was a corresponding delay in the assembly of continents and their cratonic roots (Condie and others, 2009, 2011), the production of S-type granites (Chappell and White, 2001), and the differentiation of complex pegmatites (Černý and others, 2012). The Hadean mineralogical timeline in this paper reflects this perspective, but it may be incorrect.

A number of researchers have proposed the alternative viewpoint that plate tectonics, continent formation, and S-type granites were all well established by 4.3 Ga. Oxygen isotope data from Jack Hills detrital zircons have been used to infer that some continental crust formed by convergent margin magmatism as early as 4.5 Ga, with continuous continent production throughout the subsequent Hadean Eon (Harrison and others, 2005, 2008; Watson and Harrison, 2005; Ushikubo and others, 2008; Harrison, 2009). Rollinson (2008), however, has suggested that Jack Hills zircons might have originated through hydrous partial melting of hornblende gabbros and consequent production of granitic melt. Nutman and Heiss (2009), furthermore, posit that the relatively cool observed formation temperatures of zircons implied by oxygen isotope data could point to late-stage crystallization in melts that were initially much hotter. And, even if Jack Hills zircons point to localized crustal granite, Bennett and others (2010) used Hf and ^{142}Nd isotopic signatures from Eoarchean rocks from southwest Greenland and China to argue against the generation of significant volumes of Hadean continental crust. Indeed, Kemp and others (2010) proposed that early Earth possessed a relatively thick mafic crust, resulting from consolidation of the magma ocean, which experienced only localized melting to produce modest volumes of granitoid that hosted Earth's oldest-known zircon crystals.

Intriguing, if controversial, evidence for the Hadean formation of continental crust and its associated diverse mineralogy also comes from suites of mineral inclusions, including quartz, muscovite, and K-feldspar, found in some of the oldest known zircons (Hopkins and others, 2008, 2010). This assemblage, coupled with a relatively low formation temperature and pressure based on zircon geothermometry (Watson and Harrison, 2005), was inferred by Hopkins and coworkers to represent an S-type granite source for the zircon crystals [though see Rasmussen and others (2011) for an alternative interpretation].

CONCLUSIONS

Much work remains to be done, both in terms of adding minerals that may have been initially excluded (for example, if it can be demonstrated unambiguously that modern-style plate tectonics and/or extensive continental landmasses occurred significantly prior to 4 Ga, or if new Eoarchean samples become available), as well as deleting phases (for example, if thermochemical modeling restricts the redox stability of specific minerals). Furthermore, this treatment does not delve into other aspects of mineral evolution—changes in near-surface mineralogy through time that include distinctive mineral associations; compositional ranges of major, minor, and trace

elements, as well as their stable isotopes; and the size and morphological character of mineral grains. Nevertheless, it is hoped that this preliminary list of 420 proposed Hadean Eon minerals (tables 1 and 2) will serve as a starting point for a more expansive discussion of Earth's paleomineralogy in the context of its earliest mineral-forming processes.

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