

## An evolutionary system of mineralogy, Part VI: Earth's earliest Hadean crust (>4370 Ma)

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### ABSTRACT

Part VI of the evolutionary system of mineralogy catalogs 262 kinds of minerals, formed by 18 different processes, that we suggest represent the earliest solid phases in Earth's crust. All of these minerals likely formed during the first tens of millions of years following the global-scale disruption of the Moon-forming impact prior to ~4.4 Ga, though no samples of terrestrial minerals older than ~4.37 Ga are known to have survived on Earth today. Our catalog of the earliest Hadean species includes 80 primary phases associated with ultramafic and mafic igneous rocks, as well as more than 80 minerals deposited from immiscible S-rich fluids and late-stage Si-rich residual melts. Earth's earliest crustal minerals also included more than 200 secondary phases of these primary minerals that were generated by thermal metamorphism, aqueous alteration, impacts, and other processes. In particular, secondary mineralization related to pervasive near-surface aqueous fluids may have included serpentinization of mafic and ultramafic rocks, hot springs and submarine volcanic vent mineralization, hydrothermal sulfide deposits, zeolite and associated mineral formation in basaltic cavities, marine authigenesis, and hydration of subaerial lithologies. Additional Hadean minerals may have formed by thermal metamorphism of lava xenoliths, sublimation at volcanic fumaroles, impact processes, and volcanic lightning. These minerals would have occurred along with more than 180 additional phases found in the variety of meteorites that continuously fell to Earth's surface during the early Hadean Eon.

**Keywords:** Philosophy of mineralogy, classification, mineral evolution, Hadean Eon, igneous rocks, aqueous alteration, magma ocean, mineral networks

### INTRODUCTION

The evolutionary system of mineralogy is an effort to place the >5700 mineral species approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC; <https://rruff.info/ima>, accessed 17 September 2021) into their historical and paragenetic contexts (Hazen 2019; Cleland et al. 2021; Hazen and Morrison 2022; Hazen et al. 2022). Parts I through V of the system detailed almost 300 species that occur as primary and secondary phases in meteorites (Hazen and Morrison 2020, 2021a; Morrison and Hazen 2020, 2021; Hazen et al. 2021). Thanks to decades of intensive mineralogical investigations, these earliest stages of mineral evolution are well documented.

An important aspiration of the evolutionary system of mineralogy has been to enumerate "historical natural kinds," which ideally represent "genuine divisions of nature" that arose through well-defined historical processes (Boyd 1991, 1999; Hawley and Bird 2011; Magnus 2012; Khalidi 2013; Ereshefsky 2014; Godman 2021; Cleland et al. 2021). In most instances, we attempt to classify mineral natural kinds on the basis of the distinctive combinations of chemical and physical attributes of natural specimens—properties that arose as a consequence of numerous different paragenetic modes (Hazen and Morrison 2022). Thus, for example, the trace elements, isotopes, fluid and solid inclusions, morphologies, petrologic contexts, and other attributes of pyrite

(FeS<sub>2</sub>) from hydrothermal vein deposits are strikingly different from pyrite formed by authigenesis or biogenic processes (Gregory et al. 2019)—characteristics that point to more than 20 natural kinds of pyrite (Hazen and Morrison 2022). The evolutionary system is based on those diagnostic, information-rich aspects of mineral specimens, thus complementing standard protocols of the IMA-CNMNC, which define mineral "species" based on unique combinations of major element chemical composition and idealized atomic structure (e.g., Burke 2006; Mills et al. 2009; Schertl et al. 2018; Hatert et al. 2021; Hazen 2021; Hawthorne et al. 2021).

Because the evolutionary system focuses on the changing diversity and distribution of minerals through space and time, it considers any solid phases that likely occurred during the formation and evolution of Earth's near-surface environment. While many of the most ancient minerals are preserved in meteorites, others, including nebular ices and the earliest phases that composed the terrestrial crust, are not. Here we focus on those hypothetical first solid phases formed at or near Earth's surface after its initial accretion and differentiation (>~4.56 Ga), as well as the earliest minerals to condense following the postulated catastrophic Moon-forming event at >4.4 Ga and its dynamic aftermath. No known terrestrial minerals survive from Earth's first 190 million years; the oldest reported sample is a detrital zircon grain from 4.374 ± 0.006 Ga (Valley et al. 2014). Consequently, this part of the evolutionary system will remain the most speculative stage of our planet's mineral evolution. Barring the discovery of meteorites ejected from Earth's surface during the >100-million-year window before the Moon-forming impact or from the period of

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initial cooling in the few tens of millions of years after that event (Armstrong et al. 2002; Crawford et al. 2008; Bellucci et al. 2019), the crustal mineralogy of the earliest Hadean Eon will remain a theoretical pursuit (Hazen 2013; Morrison et al. 2018; Hazen and Morrison 2021b).

In spite of this lack of tangible evidence of Earth's earliest Hadean mineralogy, convincing constraints are provided by insights from experimental petrology, isotope geochemistry, and theoretical modeling of magma ocean behavior, coupled with observations of the primitive mineralogy of Mars, Mercury, the Moon, and other rocky objects of the solar system. Accordingly, in this contribution, we offer a hypothetical introduction to Earth's earliest mineralogy—an enigmatic subject that must have unfolded in at least two major episodes.

The initial accretion of Earth and other planets occurred >4.56 Ga ago during the solar nebula's first several million years (Burkhardt et al. 2011; Budde et al. 2016; Kruijer et al. 2017; Desch et al. 2018), followed by a prolonged period of differentiation and crustal formation (Moynier et al. 2010; Kruijer et al. 2014; Badro and Walter 2015; Trønnes et al. 2019). In many respects, the earliest terrestrial minerals must have mirrored the ~120 primary and secondary asteroidal phases found in the mafic and ultramafic lithologies of stony achondrite meteorites, which represent fragments of crusts and mantles from the earliest differentiated planetesimals of the solar system (>4.55 Ga; Morrison and Hazen 2021; Hazen and Morrison 2021a). It is also likely that additional mineralogical diversity emerged through varied fluid-rock reactions in the Hadean crust, as well as alteration of subaerial deposits by impacts, evaporation, lightning, and photo-reactions, as the earliest Earth developed a dense atmosphere and dynamic hydrosphere (Abe 1993; Wilde et al. 2001; Mojzsis et al. 2001; Schaefer and Fegley 2010; Zahnle et al. 2010; Elkins-Tanton 2011; Hazen and Morrison 2022).

A second major episode of *de nova* mineralization followed cooling of the globe-spanning magma ocean that was a consequence of the Moon-forming impact at >4.4 Ga. That dramatic time of mineral obliteration was a prelude to an extended period of crustal solidification and the earliest effects of aqueous and thermal alteration—mineral-forming processes that are the focus of this contribution.

### THE MOON-FORMING EVENT AND EARTH'S PRIMORDIAL MAGMA OCEAN

Models of early Earth suggest that a combination of thermal inputs from incessant large impacts, the decay of short-lived radioactive elements, and the heat of core formation (Solomon 1979; Wetherill 1990; Tonks and Melosh 1993; Righter and Drake 1999; Elkins-Tanton 2008, 2012; Lebrun et al. 2013; Tucker and Mukhopadhyay 2014), as well as significant tidal heating following the Moon's formation (Zahnle et al. 2007) and the blanketing effects of a dense early atmosphere (Matsui and Abe 1986), may have led to multiple regional magma lake or global magma ocean events. Here we focus primarily on mineralogical consequences during the first tens of million years following the Moon-forming event, which was the largest of these postulated major disruptions.

Scenarios for the Moon's origin rely on the catastrophic collision between proto-Earth and a smaller planet-sized body at >4.4 Ga (Stevenson 1987; Canup and Asphaug 2001; Čuk and

Stewart 2012; Barr 2016; Young et al. 2016; Barboni et al. 2017; Thiemens et al. 2019). The timing of this event is a matter of considerable debate. Barboni et al. (2017) propose that Moon formation occurred at ~4.51 Ga, based primarily on U-Pb and Hf isotopic systematics. However, the absence of variations in lunar  $^{182}\text{W}/^{184}\text{W}$  attributable to the decay of short-lived  $^{182}\text{Hf}$  suggests that this age is an upper limit (R. Carlson, personal communications, 29 September 2021). Other researchers favor a significantly younger Moon, with the lower age limit constrained by the oldest known zircon grains at ~4.37 Ga (Valley et al. 2014). For example, Carlson et al. (2014) and Borg et al. (2015) cite the preponderance of lunar crustal ages <4.39 Ga as evidence for an origin event close to 4.4 Ga—results that are amplified by estimates of the age of a lunar magma ocean (Borg et al. 2019). Rather than assuming a specific age for the Moon's formation, we consider a range of possible dates:  $4.45 \pm 0.06$  Ga. Our analysis, therefore, focuses on plausible terrestrial minerals formed prior to the oldest known zircon grain.

Whatever the exact age of the Moon, the lunar origin event temporarily destroyed Earth's crustal mineralogy. A leading hypothesis for the Moon's formation invokes a high-energy, high-angular-momentum impact of a Mars-sized object and subsequent formation of a synestia—an energetic, planetary-scale structure of vaporized material that exceeded Earth's corotation limit, thus ultimately forming one or more companion bodies (Lock et al. 2018, 2020). Such a violent scenario is consistent with some models of Earth-Moon orbital dynamics while explaining similarities in the chemical and isotopic compositions of the two bodies. In all collisional models, the Moon-forming impact obliterated all traces of Earth's prior near-surface mineralogy.

The uncertain crystallization history of Earth's magma ocean can be understood in part by observations and modeling of well-preserved vestiges of the Moon's compositionally similar magma ocean. Most models of lunar magma ocean cooling and solidification favor an initial period of equilibrium crystallization because of inefficient crystal-liquid separation in a turbulent convecting magma body (Tonks and Melosh 1990; Snyder et al. 1992; Elardo et al. 2011). This interval of equilibrium crystallization was followed by the gravitationally driven formation of concentric cumulate layers and consequent chemical fractionation. Denser Mg-rich olivine cumulates, then olivine plus Mg-rich orthopyroxene crystals, sank to the base of the magma ocean, with corresponding enrichment of the residual magma ocean in Ca, Fe, Al, Ti, Si, and several minor elements (Tonks and Melosh 1990; Longhi et al. 2010; Elkins-Tanton et al. 2011; Lin et al. 2017). As cooling and solidification progressed, less dense calcic plagioclase crystallized and floated to form the anorthositic mountains of the lunar highlands (Warren et al. 1983; Norman et al. 2003; Arai and Maruyama 2017). In all viable lunar models, later stages of fractional crystallization of the residual magma ocean resulted in divergent compositions, including the crustal accumulation of KREEP basalt [i.e., enriched in potassium (K), rare earth elements (REE), and phosphorus (P)] and localized silicic lithologies (Warren et al. 1983; Chevrel et al. 1999; Wieczorek and Zuber 2001; Jolliff et al. 2006, 2011; Yamamoto et al. 2012).

The evolution of Earth's magma ocean may have paralleled that of the Moon in its broad outlines, but important differences prevailed as a consequence of the contrasting sizes and associated

pressure effects of Earth and Moon, coupled with their differing volatile compositions. In particular, while the Moon is not completely dry (Saal et al. 2008; Hui et al. 2013), the average water content of lunar magmas (a few hundred parts per million) was likely at least an order of magnitude less than that of Hadean terrestrial magmas (e.g., Moore 1970; Kuritani et al. 2014) because of early escape of volatiles from the Moon's weaker gravitational field. In addition, magma ocean pressures in the Moon did not exceed 4 GPa, which is an order of magnitude less than that of Earth's postulated magma ocean (e.g., Deng et al. 2020).

Competing models for Earth's magma ocean solidification differ in significant ways. Some hypotheses favor a prolonged period of equilibrium crystallization in a dynamically convecting mantle (Solomatov et al. 1993; Solomatov and Stevenson 1993a, 1993b, 1993c). Other scenarios suggest that Earth's mantle developed mineralogical and compositional stratification early in the solidification process (Abe 1993, 1997; Pilchin and Eppelbaum 2012), perhaps as a consequence of a Hadean "stagnant lid" (O'Neill and Debaille 2014; Ernst et al. 2016), which for a time would have significantly reduced mantle convection. Such an early stratification could help to explain the observed nonchondritic distribution of isotopes derived from short-lived radioactive isotopes (Boyett et al. 2003; Boyett and Carlson 2005, 2006; O'Neil et al. 2008; Brown et al. 2014). Subsequently, gravitationally unstable cumulates of mantle silicate minerals may have overturned to form more stable layered configurations that were resistant to the onset of large-scale thermal convection (Elkins-Tanton 2008, 2012; Schaefer and Elkins-Tanton 2018).

The timing of magma ocean solidification was probably rapid in the context of Hadean chronology, perhaps no more than a few million years (Abe 1997; Solomatov 2000, 2007), though rates of planetary cooling were highly dependent on atmospheric composition and density (Lebrun et al. 2013). Elkins-Tanton (2008) calculates that 98% of mantle magma ocean solidification occurred within 5 million years under most postulated initial conditions of atmosphere and volatile composition, with clement surface conditions developing within a few tens of millions of years. Such a short solidification interval points to the possibility of repeated magma lake or ocean events following a sequence of large (>100 km diameter) impacts over hundreds of millions of years (Marchi et al. 2014; Evans et al. 2018).

#### EARTH'S EARLIEST CRUSTAL MINERALOGY

A central objective of this contribution is to suggest a plausible mineralogy of Earth's earliest crust, prior to 4.37 Ga. In this regard, the details of magma ocean crystallization in Earth's mantle, such as the extent of large-scale stratification, crystal settling, chemical fractionation, and mantle overturn, may not be critical. Even details of the bulk composition of Earth, for example, whether it was close to chondritic or some fractionated variant (Caro et al. 2003; Caro and Bourdon 2010; DePaolo 2013), is likely of secondary importance to estimates of early Hadean crustal mineralogy. Mafic lithologies (i.e., basalt and gabbro) and their primary minerals would have dominated any plausible stable near-surface scenario, while late-stage residual magmatic fluids enriched in incompatible elements inevitably led to a modest degree of mineralogical diversity.

In developing our list of Earth's earliest minerals, we have made four assumptions about the near-surface Hadean world:

1. Most near-surface primary mineralization was the consequence of widespread volcanic activity and associated intrusive rocks.
2. A significant fraction of Earth's surface (far more than today's world) was covered by a globe-spanning water ocean prior to 4.37 Ga.
3. Some volcanic terrains breached the ocean surface, resulting in significant areas of dry land (though far less than today's world).
4. A dynamic atmosphere rich in CO<sub>2</sub> and H<sub>2</sub>O featured rain, lightning, and other surface interactions.

The resulting hypothetical inventory of 262 early Hadean minerals (Online Materials' Table OM1 and associated Read-Me file) is based on two principal criteria. First, we look to asteroidal mineralogy preserved in stony achondrite meteorites, which provide an informative baseline. Primary mafic and ultramafic igneous minerals and their thermal, aqueous, and shock alteration products in achondrites point to 114 likely early Hadean minerals in Earth's crust (Morrison and Hazen 2021; Hazen and Morrison 2021a, 2022).

Of the 262 minerals that we propose formed on the Hadean Earth, 148 mineral species are not yet known from meteorites. These phases were plausibly formed by dynamic processes in Earth's shallow crust, hydrosphere, and atmosphere. We list more than 60 minerals, including 39 not yet found in meteorites, that were associated with volcanoes by condensation at fumaroles, precipitation in zeolite-bearing basalt cavities, and thermal alteration in lava-borne xenoliths. We speculate that aqueous alteration in Earth's shallow crust produced 106 minerals (at least 67 of which have not been identified in meteorites) in hydrothermal veins, at marine and terrestrial hydrothermal vents and geysers, in zones of serpentinization, and by low-temperature alteration. An additional 110 species (44 appearing for the first time) may have arisen from processes on the terrestrial surface, including authigenesis, freezing of aqueous solutions, impacts, lightning, evaporation, and photo-reactions with sunlight (Table 1).

It is important to note a large number of possible early Hadean minerals that we do not include in this speculative inventory. For example, we do not list mineral species that are: (1) not yet known from achondrite meteorites and (2) that are relatively rare on Earth today (i.e., minerals known from fewer than 20 localities; <https://mindat.org>, accessed 6 September 2021). The gyrolite group of phyllosilicates, none of which is known from meteorites, is a case in point. Gyrolite [NaCa<sub>16</sub>Si<sub>23</sub>AlO<sub>60</sub>(OH)<sub>8</sub>·14H<sub>2</sub>O] is found in association with basalt-hosted zeolite minerals or hydrothermally altered lithologies in more than 100 localities (<https://mindat.org>, accessed 16 September 2021) and therefore it is included in our inventory. However, other less common members of the gyrolite group with similar compositions and parageneses, including reyerite [(Na,K)<sub>2</sub>Ca<sub>14</sub>(Si,Al)<sub>24</sub>O<sub>58</sub>(OH)<sub>8</sub>·6H<sub>2</sub>O], truscottite [(Ca,Mn)<sub>14</sub>Si<sub>24</sub>O<sub>58</sub>(OH)<sub>8</sub>·2H<sub>2</sub>O], and tungusite [Ca<sub>4</sub>Fe<sub>2</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>6</sub>], are known from fewer than 10 localities and are not included. In addition, our list of the earliest Hadean minerals does not include species with several rare elements, including Li, Be, B, Ga, Ge, Se, Rb, Sr, Y, Cd, Tl, Pb, and U. These criteria reflect the relatively restricted physical

**TABLE 1.** Distribution of 262 plausible early Hadean (>4.37 Ga) minerals from 18 near-surface formational environments

Formational environment	No. species <sup>a</sup>	No. cumulative <sup>b</sup>	Refs <sup>c</sup>
Primary igneous minerals	83		
1. Ultramafic rocks (UMA)	41	41	1, 2
2. Mafic rocks (MAF)	39	55	2–4
3. Silica-saturated rocks (SIL)	32	67	4–8
4. Anorthosites (ANO)	15	67	2, 3
5. Volcanic fumaroles (FUM)	23	83	9, 10
Hydrothermal minerals	98		
6. Minerals precipitated in basalt cavities (ZEO)	27	107	11
7. Hydrothermal vein minerals (HYD)	54	139	12
8. Terrestrial hot springs and geysers (HSG)	30	145	11, 13, 14
9. Seafloor hydrothermal vents (SHT)	32	150	15, 16
Thermal or aqueous alteration of prior minerals	106		
10. Thermal metamorphism of xenoliths (XEN)	14	152	2, 9
11. Serpentinization (SER)	46	178	16–18
12. Low-temperature aqueous alteration (LTA)	67	199	11, 13
Surficial mineral-forming processes	109		
13. Authigenesis (AUT)	39	201	11, 13, 19
14. Freezing of aqueous solutions (ICE)	3	204	20
15. Terrestrial impacts (IMP)	41	243	21
16. Lightning (LIG)	12	251	9, 22, 23
17. Evaporites (EVA)	14	260	24, 25
18. Photo-reactions with sunlight (PHO)	5	262	26, 27

Notes: References: 1 = Johannsen (1938); 2 = Philpotts and Ague (2009); 3 = Johannsen (1937); 4 = Rollinson (2007); 5 = Johannsen (1932); 6 = Valley et al. (2002); 7 = Hamilton (2007); 8 = Harrison (2008); 9 = Grapes (2006); 10 = Vergasova and Filatov (2016); 11 = Deer et al. (2004); 12 = Mungall and Naldrett (2008); 13 = Wilson (2013); 14 = Pirajno (2020); 15 = Haymon and Kastner (1981); 16 = Palandri and Reed (2004); 17 = Lowell and Rona (2002); 18 = Holm et al. (2015); 19 = Bowles et al. (2011); 20 = Aquilano et al. (2021); 21 = Tschauer (2019); 22 = Essene and Fisher (1986); 23 = Hess et al. (2021); 24 = Holser (1979); 25 = Boggs (2006); 26 = Roberts et al. (1980); 27 = Kim et al. (2013).

<sup>a</sup> Detailed lists of minerals and their paragenetic modes appear in Online Materials<sup>1</sup> Table OM1.

<sup>b</sup> The cumulative total of minerals. Note that many mineral species form by more than one paragenetic process (Hazen and Morrison 2022).

<sup>c</sup> General references for mineral formation environments include Anthony et al. (1990–2003); Deer et al. (1982–2013); Hazen and Morrison (2022); and Hazen et al. (2022). See also <https://ruffinfo/ima> and <https://mindat.org>, and references therein (accessed 7 August 2021).

and/or chemical conditions of formation that are typical of many rare mineral species (Hazen and Ausubel 2016)—conditions we suggest that were not present on Earth prior to 4.37 Ga.

We do not include minerals known exclusively or primarily from exotic achondrite lithologies (Hazen and Morrison 2021a; Morrison and Hazen 2021; Rubin and Ma 2021), including highly reduced phases in enstatite chondrites [e.g., daubréelite (FeCr<sub>2</sub>S<sub>4</sub>); oldhamite (CaS); wasonite (WS)]; rare phosphates and other minerals found as meteorite phases exclusively in angrites [e.g., celsian (BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>); kirschteinite (CaFeSiO<sub>4</sub>); kuratite (Ca<sub>3</sub>Fe<sub>3</sub>TiO<sub>2</sub>Si<sub>4</sub>Al<sub>2</sub>O<sub>18</sub>); matyhite [Ca<sub>9</sub>(Ca<sub>0.5</sub>□<sub>0.5</sub>)Fe(PO<sub>4</sub>)<sub>7</sub>]; tsangpoite [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(SiO<sub>4</sub>)]; or achondrite phases found only in urelites [eskolaite (Cr<sub>2</sub>O<sub>3</sub>); suessite (Fe<sub>3</sub>Si)]. Similarly, we omit rare minerals in silicate inclusions in iron meteorites [armalcolite [(Mg,Fe)Ti<sub>2</sub>O<sub>5</sub>]; kaersutite (NaCa<sub>2</sub>Mg<sub>3</sub>AlTiSi<sub>6</sub>Al<sub>2</sub>O<sub>24</sub>); yagiite (NaMg<sub>2</sub>AlMg<sub>2</sub>Si<sub>12</sub>O<sub>30</sub>)]; phases known only as alteration products of calcium-aluminum inclusions [goldmanite (Ca<sub>3</sub>V<sub>2</sub>SiAl<sub>2</sub>O<sub>12</sub>); hutcheonite (Ca<sub>3</sub>Ti<sub>2</sub>SiAl<sub>2</sub>O<sub>12</sub>)]; or any of more than a dozen rare oxides and silicates known only from the Allende CV chondrite [Hazen and Morrison 2021a; Rubin and Ma 2021; e.g., adrianite (Ca<sub>12</sub>Al<sub>4</sub>Mg<sub>3</sub>Si<sub>7</sub>O<sub>32</sub>Cl<sub>6</sub>); beckettite (Ca<sub>2</sub>V<sub>6</sub>Al<sub>6</sub>O<sub>20</sub>); chihuahuaite

[(Fe,Mg)Al<sub>12</sub>O<sub>19</sub>]; coulsonite [(Fe,Mg)V<sub>2</sub>O<sub>4</sub>], wadalite (Ca<sub>6</sub>Al<sub>5</sub>Si<sub>2</sub>O<sub>16</sub>Cl<sub>3</sub>)].

With the exception of 14 plausible sanidinite facies minerals found in thermally metamorphosed xenoliths of mafic and ultramafic lithologies, we do not include metamorphic minerals, such as those known exclusively from regional metamorphic or skarn/contact metamorphic deposits. Thus, for example, minerals of the aenigmatite, osumillite, pumpellyite, scapolite, or vesuvianite groups are not represented in our earliest terrestrial inventory. Such phases require the formation of parent lithologies, then burial (in some instances by subduction) and alteration of those rocks, and subsequent uplift and near-surface exposure (Philpotts and Ague 2009; Brown 2013). While it is plausible that such mineral-forming sequences occurred early in Earth's history, we defer listing most metamorphic minerals until later in the Precambrian, when the advent of significant continental formation and orogenesis related to plate tectonics enriched mineral inventories. Of special note in this regard, although localized carbonate minerals likely formed in modest volumes at hot springs and in association with the carbonation of mafic minerals exposed to the early CO<sub>2</sub>-rich atmosphere, we do not list the more than 350 minerals associated with contact metamorphism of carbonates and associated skarn deposits (Hazen and Morrison 2022, Supplementary Table 1 therein).

A distinctive characteristic of Earth's crustal evolution has been the emplacement of highly evolved igneous lithologies that likely represent multiple stages of crystallization, partial melting, and fractionation. Among these rock types are carbonate-bearing kimberlites and carbonatites; complex granite pegmatites, noteworthy for minerals of rare elements such as B, Be, Li, and REE; peraluminous igneous rocks; and Si-depleted alkali igneous suites (agpaite lithologies) that are exceptionally enriched in Na and K, with corresponding development of feldspathoid minerals (Johannsen 1932, 1937; London 2008; Philpotts and Ague 2009; Bea et al. 2013; Furnes and Dilek 2017; Marks and Markl 2017; Ackerson et al. 2021). We suggest that the diverse mineral species unique to these distinctive igneous rocks did not first appear until later in the Hadean Eon (Hazen and Morrison 2022). Therefore, they will be considered in Part VII of this series (Hazen et al. 2023).

We identify 262 kinds of minerals that plausibly formed within a few tens of millions of years after the Moon-forming event (Online Materials<sup>1</sup> Table OM1; see also the Supplementary “Read-Me” file). Of these minerals, 236 are valid species with names approved by the IMA-CNMNC. However, in 26 instances, we employ names that deviate from IMA conventions (indicated by blue highlights in Online Materials<sup>1</sup> Table OM1). Four of these unapproved minerals, including silica glass, basaltic glass, impact-produced amorphous CaSiO<sub>3</sub>, and maskelynite (impact plagioclase glass), are non-crystalline phases, while two are as yet poorly characterized and unnamed impact Mg-Fe silicates known only from meteorites (Ma et al. 2019a, 2019b), but likely also present on the perpetually blasted early Hadean surface.

In 18 cases, we lump two or more closely related minerals into one mineral “root kind” (Hazen et al. 2022). In some cases, we employ unapproved names for petrologically familiar solid solutions. “Biotite” includes various Fe-bearing dark micas with the general formula [K(Mg,Fe<sup>2+</sup>)<sub>3–x</sub>Al<sub>x</sub>(Al<sub>1+x</sub>Si<sub>3–x</sub>O<sub>10</sub>(OH)<sub>2</sub>] (Fleet 2003; Figure 172 therein). “Chlorite” refers to all Mg-Fe-Al-dominant members of the chlorite group, most commonly

clinochlore  $[\text{Mg}_3\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8]$ , but possibly extending to chamosite  $[(\text{Fe}^{2+}, \text{Mg}, \text{Al}, \text{Fe}^{3+})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH}, \text{O})_8]$  and sudoite  $[\text{Mg}_2\text{Al}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8]$  in some Hadean settings, as well (Deer et al. 2009). We lump greenalite  $[(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4]$  with cronstedtite  $[(\text{Fe}^{2+}, \text{Fe}^{3+})_3(\text{Si}, \text{Fe}^{3+})_2\text{O}_5(\text{OH})_4]$ , as both are Fe-dominant trioctahedral serpentine group minerals and they appear to form a continuous solid solution.

“Hornblende” encompasses a range of aluminous calcic clin amphiboles, including members of the tschermakite, hastingsite, and pargasite groups with the general formula  $[(\square, \text{Na})\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Si})_2\text{Si}_6\text{O}_{22}(\text{OH}, \text{O})_2]$  (Deer et al. 1997, Figure 279 therein). “Melilite” refers to intermediate members of the akermanite  $[\text{Ca}_2\text{MgSi}_2\text{O}_7]$ -gehlenite  $[\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_7]$  series (Deer et al. 1986, Figure 137 therein); “plagioclase” denotes intermediate members of the albite  $(\text{NaAlSi}_3\text{O}_8)$ -anorthite  $(\text{CaAl}_2\text{Si}_2\text{O}_8)$  series (Deer et al. 2001, Figure 1 therein); and we recognize the intimate exsolution of K- and Na-rich alkali feldspars as “perthite.” We lump fluorapatite, chlorapatite, and hydroxylapatite into “apatite”  $[\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})]$ ; monazite-(Ce), monazite-(La), monazite-(Nd), and monazite-(Sm) into “monazite”  $[(\text{REE})(\text{PO}_4)]$ ; and allanite-(Ce), allanite-(La), allanite-(Nd), and allanite-(Y) into “allanite”  $[\text{Ca}(\text{Y}, \text{REE})\text{Ce}(\text{Al}_2\text{Fe}^{2+})(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})]$ . Similarly, we use root names for nine zeolite mineral groups: chabazite, clinoptilite, erionite, faujasite, ferrierite, heulandite, levyne, philipsite, and stilbite (Deer et al. 2004). Finally, in our system, we use “orthoestatite” rather than “enstatite” to make a clear distinction from clinoenstatite (all of which are  $\text{MgSiO}_3$ ).

### MINERALOGY OF THE EARLY HADEAN EON (>4.37 Ga): PRIMARY IGNEOUS PHASES

In the following sections, we consider 18 terrestrial formational environments for 262 plausible early Hadean minerals (Table 1; Online Materials<sup>1</sup> Table OM1). In each subsection, the numbers and 3-letter acronyms in parentheses correspond to the 18 numbered rows in Table 1, where they appear in the same order.

#### 1. Ultramafic rocks (UMA)

The initial upper mantle lithologies of Earth’s crystallizing magma ocean were ultramafic rocks, defined as igneous rocks composed predominantly of mafic minerals and lacking significant feldspars or feldspathoids (Johannsen 1938; Dick 1989; Isley and Abbott 1999; Guilbert and Park 2007; Philpotts and Ague 2009; Lambart et al. 2016). Intrusive ultramafic rocks include olivine-dominant peridotite and pyroxene-dominant pyroxenite, which are the two major lithologies of Earth’s upper mantle. In addition, komatiite is an Mg-rich ultramafic volcanic rock with a distinctive quench texture of skeletal “spinifex” olivine, clinopyroxene, orthopyroxene, and glass—features that point to olivine as a rapidly crystallized liquidus mineral and thus suggesting a high temperature of eruption (>1650 °C), presumably when Earth had a much steeper geothermal gradient than today (Green 1975; Shore and Fowler 1999; Faure et al. 2006).

Ultramafic lithologies played a significant role in the mineralogy of Hadean Earth’s upper mantle (Rollinson 2007; Van Kranendonk et al. 2007), though significant uncertainty remains regarding the relative volumes of ultramafic vs. mafic rocks (e.g., Korenaga 2021). Dense ultramafic rocks would not have accumulated at Earth’s early Hadean surface in any significant

volumes. However, entrained xenolithic rock fragments might have been a pervasive feature of the Hadean crust. Therefore, 41 primary ultramafic minerals are included in our inventory (Online Materials<sup>1</sup> Table OM1, column UMA).

The most common primary minerals in ultramafic rocks (Johannsen 1938) include forsteritic olivine ( $\text{Mg}_2\text{SiO}_4$ ); clinopyroxene, usually Mg-rich augite, but also aegirine-augite and diopside [collectively  $(\text{Ca}, \text{Na}, \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+})_2\text{Si}_2\text{O}_6$ ]; orthopyroxene (typically close to the Mg end-member, enstatite); chromite ( $\text{Fe}^{2+}\text{Cr}_2\text{O}_4$ ); magnetite ( $\text{Fe}^{2+}\text{Fe}_3\text{O}_4$ ); spinel (ideally  $\text{MgAl}_2\text{O}_4$ , but often Cr-rich); ilmenite ( $\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$ ); and apatite. Accessory phases (Johannsen 1938) include calcic plagioclase; alkali feldspars [albite ( $\text{NaAlSi}_3\text{O}_8$ ) and orthoclase ( $\text{KAlSi}_3\text{O}_8$ )]; feldspathoids, most commonly nepheline ( $\text{NaAlSi}_3\text{O}_4$ ); zircon ( $\text{ZrSiO}_4$ ); perovskite ( $\text{CaTiO}_3$ ); rutile ( $\text{TiO}_2$ ); titanite ( $\text{CaTiSiO}_5$ ); pyrope ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ); and analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ). Sulfides, including pyrite, pyrrhotite ( $\text{Fe}_7\text{S}_8$ ), and pentlandite  $[(\text{Ni}, \text{Fe})_9\text{S}_8]$ , often associated with platinum group elements (PGE), are also common accessory minerals in ultramafic rocks, perhaps at times derived from an immiscible S- and PGE-rich fluid (e.g., Maier 2005; Collins et al. 2012). In magmas with significant water content, hydrous biopyroxenes such as hornblende, biotite, and phlogopite  $[\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2]$  may be primary phases, as well. Note that Hazen and Morrison (2022) cataloged 123 mineral species that have been identified in a variety of Precambrian ultramafic intrusive and extrusive igneous rocks, including some hydrothermally altered phases and associated polymetallic deposits. We suggest that most of those species incorporate rare elements and probably would not have appeared until significantly later in Earth’s history.

#### 2. Mafic rocks (MAF)

The dominant Hadean crustal lithologies were plagioclase-bearing mafic rocks, most commonly volcanic basalt and its intrusive equivalent, gabbro (Rollinson 2007; Van Kranendonk et al. 2007; O’Neil et al. 2008). Mafic/ultramafic mineral crusts must have formed at the surface of Earth’s magma ocean within a few million years following the synestia (e.g., Elkins-Tanton 2012; Carlson et al. 2015, 2019; O’Neil and Carlson 2017). Earth developed and sustained basaltic crusts as a consequence of adiabatic (decompression) melting of deep mantle cumulates that rose to shallower depths during overturn episodes, probably amplified by impact melting (Elkins-Tanton 2008; Griffin et al. 2014; Carlson et al. 2019). Thus, basaltic volcanism was the initial driver of significant crustal formation. Even so, the relatively cold, dense, and viscous basaltic material likely experienced repeated episodes of foundering that eliminated most vestiges of the first crust (Brown et al. 2014).

Of the several varieties of mafic rocks found on Earth today, only tholeiitic basalts associated with partial melting of depleted mantle lithosphere by mantle plumes are likely to have played a major role in the early Hadean Eon (e.g., Sharkov and Bogina 2009). By contrast, other mafic lithologies, including alkali basalts and boninites, represent later (though possibly Hadean) partial melts. For example, boninitic magmas, which are relatively enriched in Si and Mg, have been ascribed to a two-stage melting process associated with subduction and are thus of later genesis (Duncan and Green 1987).

Hazen and Morrison (2022) identified 93 mineral species docu-

mented to occur in Precambrian mafic igneous rocks. However, most of those minerals are scarce phases that incorporate one or more rare elements and, therefore, probably appeared later in the Precambrian. Here we tabulate 39 primary minerals (Online Materials<sup>1</sup> Table OM1; column MAF) that likely occurred prior to 4.37 Ga in basalt and gabbro, including calcic plagioclase (usually labradorite or bytownite), clinopyroxene (dominantly augite, but also diopside), orthopyroxene (ranging from Mg-rich enstatite to more Fe-rich bronzite or hypersthene), forsteritic olivine, hornblende, biotite, apatite, magnetite, ilmenite, spinel, and chromite (Johannsen 1937). If present, quartz (SiO<sub>2</sub>) and orthoclase were among the last minerals to crystallize. Accessory phases include zircon, pyrope, corundum (Al<sub>2</sub>O<sub>3</sub>), titanite, and graphite (C), as well as Fe sulfides (pyrite and pyrrhotite). Among the most important solid phases associated with mafic volcanism is basaltic glass. Though not an approved mineral species by the IMA-CNMNC, we recognize basaltic glass as a “mineral natural kind” (Online Materials<sup>1</sup> Table OM1).

### 3. Silica-rich rocks (SIL)

An important unanswered question is the age and extent of Earth’s earliest Si-rich (i.e., granitic/felsic) lithologies. So-called “TTG” (tonalite–trondhjemite–granodiorite) rocks with quartz and Na-Ca feldspar (though relatively minor K-feldspar), often in association with greenstone belts, represent the dominant lithologies preserved from the Eoarchean Era (Condie and Benn 2006; Hamilton 2007; O’Neil et al. 2011; O’Neill and Debaille 2014). The origin of these TTG terranes has been ascribed to partial melting of subducted oceanic basalt crust—a process that would have been enhanced by the elevated early Precambrian geothermal gradient (Martin and Moyen 2002; Martin et al. 2005; Hamilton 2007). However, subduction (and the implication of related plate tectonic processes) is not required for TTG formation. Similar partial melting events could have occurred long before modern-style subduction by the chaotic foundering and subsequent melting of mafic crust (e.g., Hamilton 2007) or by impact melting (Grieve et al. 2006). Consequently, we suggest that Si-rich lithologies, including TTG suites and other quartz-normative rocks, would have been an early and pervasive feature of Earth’s Hadean crust.

Several lines of mineralogical and geochemical evidence have been presented to bolster the idea of Hadean quartz normative rocks. In particular, the discovery of zircon grains from the early Hadean Eon (to 4.38 Ga) has raised the possibility of significant primordial granitic terrains (Valley et al. 2002, 2014; Harrison et al. 2005, 2008). A significant fraction of zircon grains older than 4.3 Ga appears to be derived from silica-rich “granitic” or acidic volcanic rocks (Cavosie et al. 2006; Pietranik et al. 2008; Kemp et al. 2010), though isotopic evidence suggests that some of these zircon specimens derive from intermediate rocks. Indeed, several authors have inferred much earlier (~4.50 Ga; i.e., pre-lunar) felsic crust from geochemical data that may point to significant fractionation of REE and Hf prior to the loss of short-lived isotopes, such as <sup>146</sup>Sm (Caro et al. 2003; Harrison 2009).

Additional evidence for early Si-rich igneous lithologies comes from the Moon and asteroids. On the Moon, localized Si-rich volcanic terrains appear to represent episodes of basalt

partial melting, perhaps related to impact melting (Chevrel et al. 1999; Jolliff et al. 2006, 2011). Similar mineralogical outliers have been associated with the partial melting of planetesimals of carbonaceous and ordinary chondrite compositions, for example, by Collinet and Grove (2020), who conducted partial melting experiments on various chondritic meteorites. Taking extra care to retain critical volatile alkali elements, they produced initial (up to ~15 wt%) low-density, high-viscosity melts enriched in silica, alumina, and alkalis. Those experimental results parallel the discovery of rare andesitic meteorites—among the oldest known achondrite meteorites at ~4.565 Ga—that presumably represent primitive igneous planetesimal crusts formed prior to significant alkali loss (Barrat et al. 2021). Such rare andesitic meteorites are interpreted as fragments of thin planetesimal crusts that overlaid the volumetrically dominant mafic mantle lithologies, which compose the vast majority of achondrite meteorites.

Analogous minor volumes of highly fractionated, localized melts must have played a role in the near-surface mineralogical diversification of early Earth (Warren 1989; Hickman and Van Kranendonk 2012; Carlson et al. 2019). The “Bowen trend” of Si-rich residues (Bowen 1928) led to Si-, Al-, and alkali-enriched magmas via 2 to 3% melting of wet peridotitic mantle, which is depleted in alkalis relative to primitive chondrites (Kinzler and Grove 1992; Baker et al. 1995). In addition, Miyazaki and Korenaga (2019a, 2019b) suggest that fractional crystallization of a magma ocean resulted in outer layers with mafic minerals relatively enriched in Fe [i.e., the “Fenner fractionation trend” (Fenner 1929)]. Harrison (2009) amplifies this theme by positing a relatively shallow magma ocean (<250 km) with forsterite crystallization and settling. The residual Si- and Al-rich melt rises to crustal depths and rapidly nucleates feldspar (Morse 1987), creating a tonalitic, high-viscosity mush that coalesced into “rockbergs of stable, felsic crust.” Harrison (2009) suggests that tonalitic crust could have appeared shortly after Earth’s formation, as well as soon after the Moon-forming event – hypotheses consistent with evidence from Hadean zircons (Harrison et al. 2008).

The primary mineralogy of early Hadean quartz normative rocks would have included quartz, plagioclase (typically Na-dominant oligoclase-andesine), orthoclase, microcline (KAlSi<sub>3</sub>O<sub>8</sub>), perthite, muscovite [KAl<sub>2</sub>(AlSi<sub>3</sub>)O<sub>10</sub>(OH)<sub>2</sub>], biotite, hornblende, arfvedsonite [NaNa<sub>2</sub>(Fe<sup>2+</sup>Fe<sup>3+</sup>)Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>], anthophyllite [□Mg<sub>7</sub>Si<sub>8</sub>O<sub>22</sub>(OH)<sub>2</sub>], almandine (Fe<sup>2+</sup>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), orthopyroxene (usually an intermediate Mg-Fe composition, such as hypersthene), clinopyroxene (including augite, diopside, and aegirine-augite), fayalite (Fe<sub>2</sub>SiO<sub>4</sub>), titanite, magnetite, apatite, zircon, rutile, ilmenite, pyrite, and pyrrhotite (e.g., Johannsen 1932).

In Online Materials<sup>1</sup> Table OM1 (column SIL) we tabulate 32 plausible minerals in early Hadean Si-rich rocks. This list is admittedly conservative. For example, we do not list the most common minerals with essential Li [spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>) or Li-rich mica], Be (beryl group), or B (tourmaline group), each of which requires significant local concentration of a rare element (London 2008). Neither do we include such common granitic accessory minerals as cassiterite (SnO<sub>2</sub>), molybdenite (MoS<sub>2</sub>), or topaz (Al<sub>2</sub>SiO<sub>4</sub>F<sub>2</sub>)—phases that we suggest first appeared later in the Hadean Eon, based in part on their absence in the Si-rich lithologies of known lunar or meteoritic samples.

#### 4. Anorthosite (ANO)

Anorthosites are distinctive igneous rocks composed almost entirely of macrocrystalline plagioclase feldspar. On Earth, most large anorthosite bodies formed during one relatively short, enigmatic interval during the Mesoproterozoic, between ~1.45 to 1.10 Ga (Philpotts and Ague 2009 and references therein). Other calcic ( $An > 80$ ) megacrystic anorthositic bodies occur as minor lithologies in some greenstone belts of the Archean Eon as early as ~3.7 Ga (Ashwal 2010). However, recent speculations regarding the possibility of extensive anorthosite bodies on early Earth, perhaps even continent-scale anorthositic development, now lost to subduction (Kawai et al. 2009; Maruyama et al. 2013; Maruyama and Ebisuzaki 2017; Dohm et al. 2018; Yoshiya et al. 2018)—deserve comment.

Hypotheses related to Hadean terrestrial anorthosites draw analogies to lunar petrology. Abundant anorthosites are among the most ancient rocks on the Moon, where these relatively low-density rocks rose diapirically to form the lunar highlands. Evidently, plagioclase crystallized in a relatively dry, low-pressure magma body, and those crystals subsequently floated to the Moon's surface to form extensive cumulates. However, comparisons of Earth and Moon in this regard are flawed. Experimental measurements have shown that plagioclase is initially negatively buoyant at high pressures in the presumed relatively hydrous silicate melts of early Earth's mantle (Condie 1982; Taylor 1982; Taylor and McLennan 1985). Plagioclase is buoyant at the relatively shallow depths (tens of kilometers) of its stability in Earth's crust; however, the high fraction of crystals and consequent increased viscosity would render significant plagioclase flotation difficult (Elkins-Tanton 2012). Furthermore, numerous phase equilibria studies demonstrate that basalt/gabbro would have been the dominant residual igneous crustal lithology derived by crystallization of a peridotitic mantle magma (e.g., Yoder 1976 and references therein), minimizing the role of anorthosite in the Hadean crust.

We conclude that plagioclase-dominant igneous rocks would have represented a minor component of Earth's early crust. However, all of the primary minerals associated with anorthosite today, including calcic plagioclase, alkali feldspar, clinopyroxene, orthopyroxene, forsterite, hornblende, biotite, zircon, titanite, magnetite, ilmenite, rutile, garnet, and pyrite (Johannsen 1937), are also present in the mineral inventories of other probable Hadean igneous minerals (Online Materials<sup>1</sup> Table OM1; column ANO). Therefore, the presence or absence of anorthosite does not significantly alter the conclusions of this compilation.

#### 5. Volcanic fumarole minerals (FUM)

In addition to the primary igneous minerals outlined above, three other processes related to volcanism may have added to early Earth's mineral diversity. Today, volcanic fumaroles and mariolitic cavities host a remarkable variety of more than 400 minerals that condense directly from hot vapors (Grapes 2006; Vergasova and Filatov 2016; Hazen and Morrison 2022). Of these species, we ascribe only 23 fumarolic minerals that incorporate relatively common elements to the earliest episodes of Hadean volcanism (Online Materials<sup>1</sup> Table OM1, column FUM). Five of these phases are silicates [albite, cristobalite ( $\text{SiO}_2$ ), fluorophlogopite, sanidine ( $\text{KAlSi}_3\text{O}_8$ ), and tridymite ( $\text{SiO}_2$ )], one is the halide fluorite ( $\text{CaF}_2$ ), two are native elements (iron and sulfur), and the remaining 10 are

sulfides known to be common in modern fumaroles with reduced S-rich vapors [bismuthinite ( $\text{Bi}_2\text{S}_3$ ), chalcocopyrite ( $\text{CuFeS}_2$ ), digenite ( $\text{Cu}_{1.8}\text{S}$ ), galena ( $\text{PbS}$ ), greenockite ( $\text{CdS}$ ), marcasite ( $\text{FeS}_2$ ), orpiment ( $\text{As}_2\text{S}_3$ ), pyrite, realgar ( $\text{AsS}$ ), and wurtzite ( $\text{ZnS}$ )].

#### 6. Basalt-hosted zeolites and other vesicle-filling minerals (ZEO)

A prominent mineralogical feature of many basaltic formations is the extensive development of zeolites and other minerals that precipitated from warm to hot fluids in vesicles. More than 80 zeolite minerals, most of them rare, have been identified (Deer et al. 2004; <https://rruff.info/ima>, accessed 6 September 2021). We include 27 vesicle-deposited minerals, including 19 of the most common basalt-hosted zeolite minerals or mineral groups (Online Materials<sup>1</sup> Table OM1, column ZEO). For example, we list analcime, chabazite, faujasite, heulandite, laumontite, natrolite, phillipsite, stilbite, and thompsonite, as possible early Hadean minerals. Other plausible ancient minerals deposited in basalt cavities include aragonite and calcite (both  $\text{CaCO}_3$ ), gyrolite, and prehnite [ $\text{Ca}_2\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ ].

#### MINERALOGICAL CONSEQUENCES OF THE EARLY ATMOSPHERE AND OCEANS

The diversity of early Earth's near-surface mineralogy must have been dramatically enriched by events related to the formation of the atmosphere and oceans. Hazen and Morrison (2022) cataloged 350 mineral species associated with a variety of plausible Hadean fluid-rock interactions, including subsurface hydrothermal deposits, serpentinization, hot springs and geysers, seafloor hydrothermal vents, low-temperature aqueous alteration, marine authigenesis, evaporite formation, and freezing. Here, we consider a subset of those minerals that may have formed within a few tens of millions of years of the Moon-forming event.

As with all near-surface minerals formed prior to ~4.50 Ga, any vestiges of Earth's pre-lunar atmosphere or oceans were lost in the Moon-forming event. What, then, was the nature and timing of the transition from the incandescent, silicate-rich synestia to a clement planet with a persistent atmosphere and oceans? Answers depend in large measure on the initial fractionation and cycling of volatile elements and molecules among several evolving reservoirs, including the convecting and cooling magma ocean, primary minerals of mafic and ultramafic rocks, condensed aqueous fluids in a variety of near-surface environments, and the enveloping gas phases of the atmosphere (e.g., Ikoma et al. 2018).

According to some models, the post-lunar magma ocean was largely devolatilized, thus transferring most  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , alkali metals, and other volatile elements/molecules to the near-surface environment (Zahnle et al. 2010). Even so, some water must have persisted in the mantle, for example, as H in nominally anhydrous minerals (Bell and Rossman 1992; Bolfan-Casanova and Keppler 2000; Kohn and Grant 2006; Tikoo and Elkins-Tanton 2017). After the synestia, additional volatiles would have been delivered to Earth's surface by a steady influx of asteroids and comets (e.g., Albarède 2009; Alexander et al. 2012). However, the relative importance of Earth's original volatile budget vs. subsequent contributions through post-lunar bombardment remains a matter of debate (Kasting and Howard 2006; Zahnle et al. 2010, 2020).

Widely cited models of the early atmosphere posit a dense

mixture primarily of CO<sub>2</sub> and H<sub>2</sub>O, with N<sub>2</sub>, H<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>S, perhaps with a surface pressure greater than 100 atm (Zahnle et al. 2010; Pilchin and Eppelbaum 2012). An added wrinkle is speculation that intense post-lunar bombardment of Earth by Fe-Ni metal-bearing inner solar system objects might have generated a correspondingly reduced atmosphere enriched in H<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub>, and thus conducive to some models of organic chemical reactions as a prelude to the origins of life (Sekine et al. 2003; Zahnle et al. 2020). However, such alteration of the atmosphere by bombardment may have significantly post-dated 4.37 Ga (Evans et al. 2018; Morbidelli et al. 2018). In any event, a dense early atmosphere would have led to consequential near-surface feedbacks. For example, water can be very soluble in silicate magmas, which can affect atmospheric composition by H<sub>2</sub>O drawdown (Schaefer and Fegley 2010).

Similarly, atmospheric CO<sub>2</sub> readily reacts with mafic minerals to form carbonates, as observed in modern-day ophiolite terrains (Sleep and Zahnle 2001; Kelemen and Matter 2008; Streit et al. 2012; Chavagnac et al. 2013; Shibuya et al. 2013; Giampouras et al. 2020; Kadoya et al. 2020). Incorporation of volatiles by near-surface rocks and magma, coupled with active convection and overturn, could have significantly increased water contents of the crust and upper mantle, ultimately leading to volcanic venting of volatiles rich in H, C, O, N, and S (Gaillard and Scaillet 2014). Even though the initial surface environment of the cooling magma ocean was too hot for the accumulation of liquid water, the primary igneous minerals outlined in the sections above would have been subject to alteration by interactions with steam and/or supercritical H<sub>2</sub>O- and CO<sub>2</sub>-bearing fluids (Zahnle et al. 1988). Therefore, we adopt the view that Hadean Earth developed an active hydrosphere, perhaps within a few million years following the synestia (Wilde et al. 2001; Mojzsis et al. 2001; Harrison 2009; Elkins-Tanton 2011).

Many uncertainties remain regarding Earth's earliest water cycle. For example, the water content of volcanic exhalations (and hence the rate of cycling through the mantle) may have been strongly dependent on atmospheric pressure. Gaillard and Scaillet (2014) suggest that at surface pressure  $\gg 1$  atm, as is postulated for Earth soon after the Moon's formation, volcanic emissions are N<sub>2</sub>- and CO<sub>2</sub>-rich, but relatively dry. By contrast, at  $\sim 1$  atm, volcanic gases are dominated by H<sub>2</sub>O, whereas surface pressures  $\ll 1$  atm favor sulfur-rich gases. If Earth's earliest atmosphere was in excess of 100 bars, then an active surface hydrological cycle may have been delayed.

Ultimately, surface cooling below 100 °C would have supported the condensation of water, resulting in a warm early ocean (Abe and Matsui 1988; Abe 1993; Schaefer and Fegley 2010; Ernst et al. 2016). Models of early Hadean oceans suggest important differences from those of today. For example, Hadean oceans were anoxic and thus likely enriched in soluble reduced ions such as Fe<sup>2+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup> compared with today's oceans (Anbar and Knoll 2002; Anbar 2008). Dissolved carbon dioxide from a dense CO<sub>2</sub>-rich atmosphere may have resulted in initially acidic conditions (Morse and Mackenzie 1998). Early Hadean oceans also probably had significantly higher salinity than modern oceans, both because they were warmer and because Earth's volatile elements (including alkali metals and halogens) were concentrated near the surface after the synestia and before the extensive formation of

crustal minerals such as alkali feldspars with Na and K (Holland 1984; Knauth 2005; Izawa et al. 2010; Zahnle et al. 2010; Charnay et al. 2017; Marty et al. 2018).

The volume and aerial extent of Earth's early oceans are also uncertain. Some researchers point to globe-spanning oceans with perhaps twice today's volume of water because of a relatively dry, hot peridotitic mantle prior to subduction-driven cycling of water; with subsequent extensive mantle hydration reduced the amount of surface waters (Jarrard 2003; Korenaga 2008; Korenaga et al. 2017; Kurokawa et al. 2018; Dong et al. 2021; Rosas and Korenaga 2021). If so, then the more voluminous early Hadean oceans would have covered almost all of Earth's surface because of less extreme topography prior to the development of felsic continents and associated orogenesis.

We conclude that by 4.37 Ga, lakes and oceans may have covered a significant fraction of Earth's surface (Wilde et al. 2001; Elkins-Tanton 2011; Dong et al. 2021), while the shallow subsurface experienced significant hydrothermal circulation (Heinrich and Henley 1989; Pirajno 2009). In the following sections, we consider more than 150 plausible minerals that may have formed through fluid-rock interactions prior to 4.37 Ga.

## 7. Hydrothermally deposited subsurface minerals (HYD)

With more than 850 documented species, subsurface hydrothermal deposits represent one of the most diverse mineral-forming environments on Earth. Hazen and Morrison (2022) identified 129 of those phases, primarily sulfides and a few arsenides of the more common transition metal elements, as well as minerals hosting PGE elements associated with ultramafic lithologies (Mungall and Naldrett 2008), as plausible Hadean species. Here we further reduce that inventory to 54 of the most abundant hydrothermal minerals (i.e., known from 20 or more localities; <https://mindat.org>, accessed 9 September 2021) that might have appeared prior to 4.37 Ga (Online Materials<sup>1</sup> Table OM1, column HYD). All of these species are known to be associated with mafic or ultramafic hydrothermal systems, and most of them are sulfides or arsenides of Fe, Ni, Cu, Co, or Zn.

## 8. Terrestrial hot springs and geysers (HSG)

The exposed volcanic surface of the Hadean world, though possibly less extensive than today, would have featured abundant subaerial hot springs and geysers that produced a range of geothermal minerals (Pirajno 2020), perhaps including the earliest terrestrial occurrences of carbonates and sulfates [e.g., anhydrite (CaSO<sub>4</sub>), aragonite, baryte (BaSO<sub>4</sub>), calcite, and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O)]. Widespread low-temperature aqueous alteration of Hadean lithologies would also have enriched early Earth's inventory of hydrous silicates, including clay minerals and zeolites (Deer et al. 2004; Wilson 2013). Online Materials<sup>1</sup> Table OM1 (column HSG) lists 30 postulated hot springs and geyser minerals that may have precipitated prior to 4.37 Ga.

## 9. Seafloor hydrothermal vents (SHT)

Earth's earliest seafloor would have been punctuated by numerous vents that emitted mineral-rich hydrothermal fluids, though the character of vent chemistry and consequent mineralization may have differed significantly from today. We suspect that compositions would have ranged, as they do today, from sulfide-dominated

“black smokers” to carbonate-bearing “white smokers” (Hekinian et al. 1980; Haymon and Kastner 1981; Palandri and Reed 2004; Schwarzenbach and Steele-MacInnis 2020). Accordingly, we list a subset of 32 relatively common minerals, primarily sulfides (19 species), as well as carbonates, sulfates, and hydrous phases that likely occurred in seafloor hydrothermal vent systems (Online Materials<sup>1</sup> Table OM1, column SHT).

### 10. Lava-hosted xenolith minerals (XEN)

A modest number of early Hadean minerals were likely formed as a consequence of high-temperature, low-pressure (sanidinite facies) metamorphism of xenoliths, which are varied lithic fragments entrained in a magma (e.g., Grapes 2006). Hazen and Morrison (2022) cataloged 127 plausible Hadean xenolith minerals. However, we suggest that only 14 oxide and silicate species would have been likely to form via sanidinite facies metamorphism of early Hadean ultramafic, mafic, and TTG xenoliths (Online Materials<sup>1</sup> Table OM1, column XEN). Furthermore, with the possible exceptions of clinoenstatite and cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ), all of these minerals also occur in one or more of the igneous rocks already discussed. Note in particular that phases derived from Al-rich sediments [corundum, mullite ( $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-3}$ ;  $x \sim 0.4$ ), sillimanite ( $\text{Al}_2\text{SiO}_5$ )] or by reaction with carbonate xenoliths [gehlenite, larnite ( $\text{Ca}_2\text{SiO}_4$ ), wollastonite ( $\text{CaSiO}_3$ )], which are commonly found in recent sanidinite facies metamorphic rocks, are not included in our inventory.

### 11. Hadean serpentinization (SER)

The serpentinization of mafic and ultramafic rocks, by which Fe- and Mg-bearing minerals are hydrated in low- to moderate-temperature (to  $\sim 400^\circ\text{C}$ ), near-surface aqueous environments, has been a significant mineral-forming process throughout Earth’s history (Moody 1976; Russell et al. 2010; Schrenk et al. 2013; Shibuya et al. 2015; Lamadrid et al. 2017; Korenaga 2021; Voosen 2021). Serpentinization played a major role in Earth’s crustal evolution by transforming ocean floor mafic and ultramafic rocks to assemblages of serpentine, brucite, magnetite, and dozens of other phases (Blais and Auvray 1990; Lowell and Rona 2002; Palandri and Reed 2004; Schrenk et al. 2013; Holm et al. 2015; Yoshiya et al. 2018). In Online Materials<sup>1</sup> Table OM1 (column SER), we list 46 minerals associated with serpentinization of the primary minerals in near-surface Hadean mafic and ultramafic lithologies (see also Johannsen 1938 for lists of common secondary minerals in these rocks). Of these phases, 24 are hydrated Mg-bearing minerals and 18 contain Fe and/or Ni.

### 12. Low-temperature aqueous alteration (LTA)

In addition to the diverse minerals formed by serpentinization and by precipitation associated with hydrothermal systems, submarine vents, hot springs, and geysers, relatively low-temperature ( $<100^\circ\text{C}$ ) aqueous alteration of Hadean mafic and ultramafic lithologies in subaerial and shallow subsurface environments may have produced scores of mineral species, most notably hydroxides, zeolites, clay minerals, and other hydrous silicates (Deer et al. 2004; Wilson 2013). In Online Materials<sup>1</sup> Table OM1 (column LTA), we catalog 67 plausible aqueous alteration phases from Earth’s first 100 million years. Note that these phases, in part, mirror minerals found in achondrite meteorites that have experienced

aqueous alteration—22 species are common to both environments (Hazen and Morrison 2021a).

### 13. Marine authigenic minerals (AUT)

Interactions of early Hadean seawater with serpentinized rocks and seafloor sediments likely produced an assemblage of authigenic phases, defined as minerals formed in situ as a consequence of direct precipitation from an aqueous solution, as opposed to aqueous alteration of prior minerals (see above), for example as a carbonate cement in detrital sediments. Following the conventions of Hazen and Morrison (2022), authigenesis refers only to the formation of minerals in low- $T$  ( $<100^\circ\text{C}$ ) shallow sedimentary or porous near-surface environments. We list 39 possible authigenic minerals (Online Materials<sup>1</sup> Table OM1, column AUT), most of which are zeolites, clays, or other hydrous phases.

### 14. Minerals formed by freezing (ICE)

The timing of Earth’s earliest polar ice caps is unknown, but localized episodes of freezing may have occurred, especially if Earth’s axial inclination was episodically greater than today. If so, then as many as three additional mineral species—ice ( $\text{H}_2\text{O}$ ), hydrohalite ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ), and ikaite ( $\text{CaCO}_3\cdot 6\text{H}_2\text{O}$ )—may have occurred in cold regions (Aquilano et al. 2021; Online Materials<sup>1</sup> Table OM1, column ICE).

## OTHER MINERAL-FORMING PROCESSES

At least four additional subaerial processes—impacts, lightening, evaporite formation, and photo-oxidation—may have added to early Earth’s mineral diversity.

### 15. Impact mineralization (IMP)

Impact mineralization would have been a pervasive feature of the Hadean landscape (e.g., Koeberl 2006). Marchi et al. (2014) proposed a bombardment model of early Earth that suggests repeated reprocessing of most of Earth’s surface by large impacts prior to 4 Ga. They posit, “No substantial, large region of the Earth’s surface could have survived untouched by impacts and associated outcomes.”

Meteorites and terrestrial rocks record shock events with peak transient temperatures and pressures that may have exceeded  $3000^\circ\text{C}$  and 100 GPa lasting several seconds (Ohtani et al. 2004; Xie et al. 2006; Tomioka and Miyahara 2017; Stöffler et al. 2018; Tables 4 through 11 therein). The mineralogical consequences of such violent events on ultramafic, mafic, and TTG lithologies are well documented through studies of dozens of shocked phases in meteorites and from terrestrial impact craters (Koeberl 2002; Tomioka and Miyahara 2017; Ma 2018; Stöffler et al. 2018; Tschauner 2019; Rubin and Ma 2021). Morrison and Hazen (2021, Table 2 therein) documented 40 impact minerals known from a range of meteorites. In Online Materials<sup>1</sup> Table OM1 (column IMP) we include 41 minerals, of which 36 are also in our inventory of meteorite minerals. Five proposed early Hadean terrestrial impact minerals are not yet known from meteorites: akaogiite ( $\text{TiO}_2$ ; El Goresy et al. 2010), maohokite ( $\text{MgFe}_2\text{O}_4$ ; Chen et al. 2019), reidite ( $\text{ZrSiO}_4$ ; Glass et al. 2002), reSITE ( $\text{TiO}_2$ ; Tschauner et al. 2020), and yoshiokaite [ $\text{Ca}_{1-x}(\text{Al},\text{Si})_2\text{O}_6$ ; Vaniman and Bish 1990]. We do not include impact-generated martensite ( $\alpha\text{-Fe,Ni}$ ) and allabogdanite [(Fe,Ni)<sub>2</sub>P], as they arise exclusively in iron

meteorites. Note also that in five instances [akimotoite-hemleyite, (Mg,Fe)SiO<sub>3</sub>; bridgmanite-hiroseite, (Mg,Fe)SiO<sub>3</sub>; periclase-wüstite or “magnesiowüstite,” (Mg,Fe)O; ringwoodite-ahrensite, (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>; and wadsleyite-asimowite, (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>] we lump pairs of isostructural species with Mg and Fe end-members because observed shock phases are typically of intermediate compositions (Morrison and Hazen 2021; Hazen et al. 2022).

Many of these impact phases are dense, high-pressure polymorphs of abundant rock-forming minerals, including olivine, pyroxene, feldspar, and spinel group oxides. The list also includes two shock-induced amorphous phases, silica glass (SiO<sub>2</sub>) and the impact plagioclase glass known as maskelynite.

An additional mineralogical consequence of large impacts would have been creation of extensive and long-lasting fracture systems that promoted hydrothermal circulation and associated fluid-rock interactions, preferential solution and mobilization of some rare elements, and mineralization (Rodriguez et al. 2005; Pirajno 2009; Osinski et al. 2013).

### 16. Lightning minerals (LIG)

Lightning, which appears to be a pervasive attribute of both terrestrial and gaseous planets with turbulent atmospheres (Williams et al. 1983; Russell et al. 2008, 2011; Lorenz 2018), is an intriguing and as yet little studied mineral-forming mechanism. In this context, lightning is best known for forming hollow branching structures of fused sediments called fulgurites (Essene and Fisher 1986; Grapes 2006; Pasek et al. 2012). These fascinating objects hold a modest inventory of 9 reported mineral species (Hazen and Morrison 2022), including such reduced phases as graphite, silicon (Si), moissanite (SiC), and schreibersite (Fe<sub>3</sub>P). However, we suspect that additional reduced lightning-generated minerals may be associated with strikes on ultramafic and mafic lithologies, notably in association with volcanic lightning (McNutt and Williams 2010; Cimarelli et al. 2014; Van Eaton et al. 2016; Cartier 2020; Smith et al. 2021). Such occurrences may incorporate mineralogical novelties (silicides, phosphides, metal alloys), which may be difficult to detect and recover. For example, the highly reducing environment generated by the influx of electrons from a lightning strike has been invoked as a possible source of prebiotic reduced P compounds (Pasek and Block 2009; Feng et al. 2021; Hess et al. 2021). Similarly, Ballhaus et al. (2017, 2018a, 2018b, 2021) suggest that enigmatic ultra-reduced phases in ophiolites, including moissanite and a variety of native elements and alloys (e.g., Al, Fe, and Si) may result from lightning strikes, in contrast to Griffin et al. (2016, 2018) and Yang et al. (2018), who argue for a deep-mantle origin of these reduced phases. Similar arguments could be extended to Hadean lightning, especially strikes associated with active volcanoes, and its effects on mafic/ultramafic rocks. Therefore, we list 12 plausible early Hadean lightning-generated minerals (Online Materials<sup>1</sup> Table OM1, column LIG).

### 17. Evaporites (EVA)

Evaporite mineralization was an inevitable consequence of land surrounded by a saline ocean. Hazen and Morrison (2022) catalog 210 prebiotic evaporite minerals; however, the great majority of those species are rare borates, halides, sulfates, or carbonates that only appear as a consequence of the evaporation of large stranded saline water bodies or brines after continent-scale landmasses

appeared (Holser 1979; Boggs 2006). We list 14 plausible early Hadean evaporite minerals, including halides [halite (NaCl); sylvite (KCl)] and carnalite (KMgCl<sub>3</sub>·6H<sub>2</sub>O)], sulfates [anhydrite; gypsum; kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O); langbeinite (K<sub>2</sub>Mg<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>); kainite [KMg(SO<sub>4</sub>)Cl·3H<sub>2</sub>O]; and polyhalite [K<sub>2</sub>Ca<sub>2</sub>Mg(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O], and carbonates [calcite; magnesite (MgCO<sub>3</sub>)], as recorded in Online Materials<sup>1</sup> Table OM1 (see column EVA).

### 18. Minerals formed by photo-reactions (PHO)

A handful of new minerals may have been formed through the effects of sunlight on prior minerals (Kim et al. 2013; Hazen and Morrison 2022). For example, pararealgar (As<sub>8</sub>S<sub>4</sub>) is a common photo-reaction byproduct of realgar, which was a likely early Hadean fumarolic mineral (Roberts et al. 1980). Of special interest are photo-oxidation reactions of reduced Fe<sup>2+</sup>, Mn<sup>2+</sup>, and Cu<sup>1+</sup> minerals, which may have produced Fe<sup>3+</sup>-, Mn<sup>3+</sup>-, Mn<sup>4+</sup>-, and Cu<sup>2+</sup>-bearing minerals long before the biologically mediated global oxygenation of the Neoproterozoic Era. For example, Kim et al. (2013) demonstrated that siderite (FeCO<sub>3</sub>) in water breaks down to ferric iron oxides [magnetite (Fe<sub>3</sub>O<sub>4</sub>) or maghemite (Fe<sub>2.67</sub>O<sub>4</sub>)] plus H<sub>2</sub> when exposed to ultraviolet light. Similarly, ramsdellite (MnO<sub>2</sub>) and digenite (Cu<sub>1.8</sub>S) are possible products of photo-oxidation. In Online Materials<sup>1</sup> Table OM1 (column PHO), we list five minerals that might have appeared through the action of sunlight on prior species.

## IMPLICATIONS

### Early Hadean mineralogical parsimony

This contribution lists 262 minerals that may have emerged on Earth prior to 4.37 Ga via one or more of 18 formation processes. The total of 534 combinations of a mineral with a formation process tabulated in Online Materials<sup>1</sup> Table OM1 represents only 5% of the 10556 combinations of 5659 mineral species formed by 57 processes recorded by Hazen and Morrison (2022) for Earth today. At least 294 meteorite species, formed by 13 pre-terrestrial processes as detailed in Parts I through V of this series, contributed an additional 455 mineral/formation combinations that would have been present at or near Earth's surface continuously since crustal solidification (Online Materials<sup>1</sup> Table OM1). Nevertheless, the diversity of Earth's mineral kingdom has expanded by an order of magnitude since the early Hadean Eon as enhanced fluid-rock interactions, plate tectonics, and biological influences have come into play.

Three factors contribute to the relative mineralogical parsimony of early Earth. First, many mineral-forming processes, notably regional metamorphism and other mechanisms associated with plate tectonics, had yet to come into play. Second, more than 40% of known mineral species require concentration of one or more rare chemical elements (Hazen and Morrison 2022); we suggest that much more time was required to achieve these degrees of element selection and localized concentration. Third, approximately 33% of all known mineral species arise exclusively through biological interactions with the environment.

Interestingly, the formation mechanisms of minerals that we ascribe to early Earth may closely parallel those of Mars during its first billion years. Like Earth, Mars probably experienced an early magma ocean with subsequent wide-ranging mafic volcanism, as

well as minor volumes of Si-, Al-, and alkali-rich partial melts. Mars had a dynamic and extensive hydrosphere, with associated mineralization by hydrothermal deposition, water-rock alteration, authigenesis, and evaporites. And, like Earth, the surface of early Mars was subject to impact mineralization, photo-oxidation, lightning, and freezing, with the addition of the full spectrum of meteorite minerals. Consequently, we suggest that Part VI of the evolutionary system of Earth's mineralogy may provide a baseline for Mars mineralogy, as well.

### Mineral network analysis

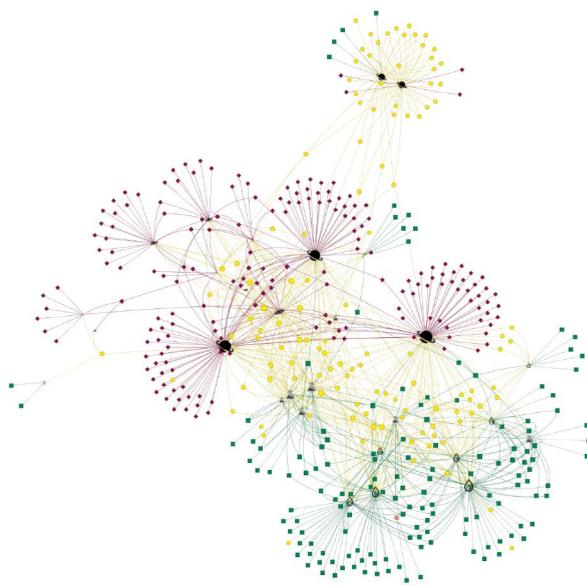
Networks are graphical representations that have the potential to reveal relationships among large numbers of minerals and their modes of formation (Morrison et al. 2017). The earliest stages of Earth's mineral evolution are illustrated in Figure 1, which is a bipartite network that illustrates relationships among 442 terrestrial and/or meteorite minerals and 31 processes by which those minerals formed. This representation of minerals that would have been found on Earth prior to 4.37 Ga includes 13 mineral-forming processes in meteorites (represented by black icons shaped as a star, disk, cloud, or planet) and 18 mineral-forming processes on early Earth (represented by black icons shaped as a volcano, droplet, planet, lightning, or lightbulb). Mineral nodes appear in three shapes and colors: red diamonds for 180 meteorite minerals not expected to form on early Earth, green squares for 148 minerals suspected to form on early Earth but not known from meteorites, and yellow circles for 114 minerals from both groups.

The topology of Figure 1 reflects the diversity of formation environments on early Earth. At the largest scale, minerals formed exclusively on Earth (green nodes) vs. those exclusively from meteorites (red nodes) are well separated, with most minerals from both environments creating a yellow band across the middle of the graph. Additional trends are also evident, with the clustering of minerals formed by various primary and secondary processes.

Figure 2 focuses on key areas of this network. As might be expected, significant overlaps between terrestrial and meteorite minerals occur among some of these various subsets of early Hadean mineralogy. For example, 36 of 41 impact-generated minerals suspected to have occurred on early Earth are also found in meteorites (Fig. 2a). Most of these phases are unique to the extremely high-temperature and high-pressure conditions of shock metamorphism. Therefore, nodes representing meteorite and terrestrial impact formation processes lie close to each other at the top of the graph but are significantly separated from most other minerals. Indeed, only five minerals, including diamond (as a stellar condensate), clinoenstatite, and cordierite (in xenoliths), connect impact minerals with other early Earth minerals.

Significant overlaps occur among many of the minerals that form as primary igneous phases in stony achondrites, and that also occur in Earth's ultramafic, mafic, and anorthositic lithologies (Fig. 2b). These minerals form a centralized cluster of yellow and green nodes. By contrast, low-temperature and low-pressure condensates ("ices") form a distinct cluster of phases in the lower left-hand side of the network (Fig. 2c). Water ice provides important connections among interstellar, circumstellar, cold asteroidal surface, and terrestrial ice environments.

Another group of minerals forms a distinct cluster of phases formed by water-rock interactions (Fig. 2d). These minerals, rep-



**FIGURE 1.** This bipartite network illustrates relationships among 442 different mineral species (represented by square- or diamond-shaped colored nodes) and 31 formation processes of those minerals (represented by various shaped black nodes). The gray lines ("edges") between these two types of nodes indicate 988 proposed combinations of a mineral species and a mode of formation. Note that each mineral is linked to one or more mode of formation, while each mode of formation is linked to one or more minerals. (Color online.)

resented by green nodes near the bottom of the graph, are linked to five droplet icons. These icons are further clustered into two lower-temperature formation processes on the right-hand side of Figure 2d (representing authigenic mineralization and low-temperature alteration) and three higher-temperature processes on the left-hand side (including serpentinization, hydrothermal vein deposition, and seafloor hydrothermal vents). Note that relatively few of these phases are also known from meteorites, so they appear as green nodes that tend to be significantly separated from the more centralized phases that share meteorite and Earth origins (i.e., yellow nodes).

### Minerals and the origins of life

The paleomineralogy of the Hadean Eon has attracted significant attention in the context of life's origins because most biogenesis models posit an origin event prior to 4.0 Ga. A wide variety of minerals have been invoked in origins scenarios, some of them not included in lists of early Hadean species (Hazen 2013). For example, phases with postulated catalytic sites such as borates, molybdates, and phosphates (Ricardo et al. 2004; Kim et al. 2016; Ziegler et al. 2018) are not in our inventories. Even if our Hadean mineral catalog is too limited, and minerals such as borates or molybdates were, in fact, present prior to 4.37 Ga, they would have been extremely minor phases with trivial total volumes. Is this lack an impediment to essential origins-of-life chemical processes?

We now realize that any chemical element that may have played a critical role in biology today was abundantly available



surface sites for biogenesis—a facet of prebiotic chemistry that has yet to be explored.

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## Endnote:

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