

1 **Revision #2—10 January 2022—Submitted to *American Mineralogist***

2
3 **An evolutionary system of mineralogy, Part VI:**
4 **Earth's earliest Hadean crust (> 4370 Ma)**

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9

10 **ABSTRACT**

11 Part VI of the evolutionary system of mineralogy catalogs 262 kinds of minerals, formed by
12 18 different processes, that we suggest represent the earliest solid phases in Earth's crust. All of
13 these minerals likely formed during the first tens of millions of years following the global-scale
14 disruption of the Moon-forming impact prior to ~4.4 Ga, though no samples of terrestrial
15 minerals older than ~4.37 Ga are known to have survived on Earth today. Our catalog of the
16 earliest Hadean species includes 80 primary phases associated with ultramafic and mafic igneous
17 rocks, as well as more than 80 minerals deposited from immiscible S-rich fluids and late-stage
18 Si-rich residual melts. Earth's earliest crustal minerals also included more than 200 secondary
19 phases of these primary minerals that were generated by thermal metamorphism, aqueous
20 alteration, impacts, and other processes. In particular, secondary mineralization related to
21 pervasive near-surface aqueous fluids may have included serpentinization of mafic and
22 ultramafic rocks, hot springs and submarine volcanic vent mineralization, hydrothermal sulfide
23 deposits, zeolite and associated mineral formation in basaltic cavities, marine authigenesis, and
24 hydration of subaerial lithologies. Additional Hadean minerals may have formed by thermal
25 metamorphism of lava xenoliths, sublimation at volcanic fumaroles, impact processes, and

26 volcanic lightning. These minerals would have occurred along with more than 180 additional
27 phases found in the variety of meteorites that continuously fell to Earth's surface during the early
28 Hadean Eon.

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32 **Keywords:** philosophy of mineralogy; classification; mineral evolution; Hadean Eon; igneous
33 rocks; aqueous alteration; magma ocean; mineral network graphs

34

INTRODUCTION

35 The evolutionary system of mineralogy is an effort to place the > 5700 mineral species
36 approved by the International Mineralogical Association's Commission on New Minerals,
37 Nomenclature, and Classification (IMA-CNMNC; <https://rruff.info/ima>, accessed 17 September
38 2021) into their historical and paragenetic contexts (Hazen 2019; Cleland et al. 2021; Hazen and
39 Morrison 2022; Hazen et al. 2022). Parts I through V of the system detailed almost 300 species
40 that occur as primary and secondary phases in meteorites (Hazen and Morrison 2020, 2021a;
41 Morrison and Hazen 2020, 2021; Hazen et al. 2021). Thanks to decades of intensive
42 mineralogical investigations, these earliest stages of mineral evolution are well documented.

43 An important aspiration of the evolutionary system of mineralogy has been to enumerate
44 "historical natural kinds," which ideally represent "genuine divisions of nature" that arose
45 through well-defined historical processes (Boyd 1991, 1999; Hawley and Bird 2011; Magnus
46 2012; Khalidi 2013; Ereshevsky 2014; Godman 2019; Cleland et al. 2021). In most instances, we
47 attempt to classify mineral natural kinds on the basis of the distinctive combinations of chemical
48 and physical attributes of natural specimens – properties that arose as a consequence of
49 numerous different paragenetic modes (Hazen and Morrison 2022). Thus, for example, the trace
50 elements, isotopes, fluid and solid inclusions, morphologies, petrologic contexts, and other
51 attributes of pyrite (FeS₂) from hydrothermal vein deposits are strikingly different from pyrite
52 formed by authigenesis or biogenic processes (Gregory et al. 2019) – characteristics that point to
53 more than 20 natural kinds of pyrite (Hazen and Morrison 2022). The evolutionary system is
54 based on those diagnostic, information-rich aspects of mineral specimens, thus complementing
55 standard protocols of the IMA-CNMNC, which define mineral "species" based on unique
56 combinations of major element chemical composition and idealized atomic structure (e.g., Burke

57 2006; Mills et al. 2009; Schertl et al. 2018; Hatert et al. 2021; Hazen 2021; Hawthorne et al.
58 2021).

59 Because the evolutionary system focuses on the changing diversity and distribution of
60 minerals through space and time, it considers any solid phases that likely occurred during the
61 formation and evolution of Earth's near-surface environment. While many of the most ancient
62 minerals are preserved in meteorites, others, including nebular ices and the earliest phases that
63 composed the terrestrial crust, are not. Here we focus on those hypothetical first solid phases
64 formed at or near Earth's surface after its initial accretion and differentiation ($> \sim 4.56$ Ga), as
65 well as the earliest minerals to condense following the postulated catastrophic Moon-forming
66 event at > 4.4 Ga and its dynamic aftermath. No known terrestrial minerals survive from Earth's
67 first 190 million years; the oldest reported sample is a detrital zircon grain from 4.374 ± 0.006
68 Ga (Valley et al. 2014). Consequently, this part of the evolutionary system will remain the most
69 speculative stage of our planet's mineral evolution. Barring the discovery of meteorites ejected
70 from Earth's surface during the > 100 -million-year window before the Moon-forming impact, or
71 from the period of initial cooling in the few tens of millions of years after that event (Armstrong
72 et al. 2002; Crawford et al. 2008; Bellucci et al. 2019), the crustal mineralogy of the earliest
73 Hadean Eon will remain a theoretical pursuit (Hazen 2013; Morrison et al. 2018; Hazen and
74 Morrison 2021b).

75 In spite of this lack of tangible evidence of Earth's earliest Hadean mineralogy, convincing
76 constraints are provided by insights from experimental petrology, isotope geochemistry, and
77 theoretical modeling of magma ocean behavior, coupled with observations of the primitive
78 mineralogy of Mars, Mercury, the Moon, and other rocky objects of the solar system.

79 Accordingly, in this contribution we offer a hypothetical introduction to Earth's earliest
80 mineralogy – an enigmatic subject that must have unfolded in at least two major episodes.

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

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

99

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

101 Models of early Earth suggest that a combination of thermal inputs from incessant large
102 impacts, the decay of short-lived radioactive elements, and the heat of core formation (Solomon
103 1979; Wetherill 1990; Tonks and Melosh 1993; Righter and Drake 1999; Elkins-Tanton 2008,
104 2012; Lebrun et al. 2013; Tucker and Mukhopadhyay 2014), as well as significant tidal heating
105 following the Moon's formation (Zahnle et al. 2007) and the blanketing effects of a dense early
106 atmosphere (Matsui and Abe 1986), may have led to multiple regional magma lake or global
107 magma ocean events. Here we focus primarily on mineralogical consequences during the first
108 tens of million years following the Moon-forming event, which was the largest of these
109 postulated major disruptions.

110 Scenarios for the Moon's origin rely on the catastrophic collision between proto-Earth and a
111 smaller planet-sized body at > 4.4 Ga (Stevenson 1987; Canup and Asphaug 2001; Cuk and
112 Stewart 2012; Barr 2016; Young et al. 2016; Barboni et al. 2017; Thiemens et al. 2018). The
113 timing of this event is a matter of considerable debate. Barboni et al. (2017) propose that Moon
114 formation occurred at ~ 4.51 Ga, based primarily on U-Pb and Hf isotopic systematics. However,
115 the absence of variations in lunar $^{182}\text{W}/^{184}\text{W}$ attributable to the decay of short-lived ^{182}Hf
116 suggest that this age is an upper limit (R. Carlson, personal communications, 29 September
117 2021). Other researchers favor a significantly younger Moon, with the lower age limit
118 constrained by the oldest known zircon grains at ~4.37 Ga (Valley et al. 2014). For example,
119 Carlson et al. (2014) and Borg et al. (2015) cite the preponderance of lunar crustal ages < 4.39
120 Ga as evidence for an origin event close to 4.4 Ga – results that are amplified by estimates of the
121 age of a lunar magma ocean (Borg et al. 2019). Rather than assuming a specific age for the
122 Moon's formation, we consider a range of possible dates: 4.45 +/- 0.06 Ga. Our analysis,
123 therefore, focuses on plausible terrestrial minerals formed prior to the oldest known zircon grain.

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

132 The uncertain crystallization history of Earth's magma ocean can be understood in part by
133 observations and modeling of well-preserved vestiges of the Moon's compositionally similar
134 magma ocean. Most models of lunar magma ocean cooling and solidification favor an initial
135 period of equilibrium crystallization, owing to inefficient crystal-liquid separation in a turbulent
136 convecting magma body (Tonks and Melosh 1990; Snyder et al. 1992; Elardo et al. 2011). This
137 interval of equilibrium crystallization was followed by gravitationally-driven formation of
138 concentric cumulate layers and consequent chemical fractionation. Denser Mg-rich olivine
139 cumulates, then olivine plus Mg-rich orthopyroxene crystals, sank to the base of the magma
140 ocean, with corresponding enrichment of the residual magma ocean in Ca, Fe, Al, Ti, Si, and a
141 number of minor elements (Tonks and Melosh 1990; Longhi et al. 2010; Elkins-Tanton et al.
142 2011; Lin et al. 2017). As cooling and solidification progressed, less dense calcic plagioclase
143 crystallized and floated to form the anorthositic mountains of the lunar highlands (Wood et al.
144 1970; Warren et al. 1983; Norman et al. 2003; Arai and Maruyama 2017). In all viable lunar
145 models, later stages of fractional crystallization of the residual magma ocean resulted in
146 divergent compositions, including the crustal accumulation of KREEP basalt [i.e., enriched in

147 potassium (K), rare earth elements (REE), and phosphorus (P)] and localized silicic lithologies
148 (Warren et al. 1983; Chevrel et al. 1999; Wieczorek and Zuber 2001; Jolliff et al. 2006, 2011;
149 Yamamoto et al. 2012).

150 The evolution of Earth's magma ocean may have paralleled that of the Moon in its broad
151 outlines, but important differences prevailed as a consequence of the contrasting sizes and
152 associated pressure effects of Earth and Moon, coupled with their differing volatile
153 compositions. In particular, while the Moon is not completely dry (Saal et al. 2008; Hui et al.
154 2013), the average water content of lunar magmas (a few hundred ppm) was likely at least an
155 order of magnitude less than that of Hadean terrestrial magmas (e.g., Moore 1970; Kuritani et al.
156 2014) owing to early escape of volatiles from the Moon's weaker gravitational field. In addition,
157 magma ocean pressures in the Moon did not exceed 4 GPa, which is an order of magnitude less
158 than that of Earth's postulated magma ocean (e.g., Deng et al. 2020).

159 Competing models for Earth's magma ocean solidification differ in significant ways. Some
160 hypotheses favor a prolonged period of equilibrium crystallization in a dynamically convecting
161 mantle (Solomatov et al. 1993; Solomatov and Stephenson 1993a, 1993b, 1993c). Other
162 scenarios suggest that Earth's mantle developed mineralogical and compositional stratification
163 early in the solidification process (Abe 1993, 1997; Pilchin and Eppelbaum 2012), perhaps as a
164 consequence of a Hadean "stagnant lid" (O'Neill and Debaille 2014; Ernst et al. 2016), which for
165 a time would have significantly reduced mantle convection. Such an early stratification could
166 help to explain the observed nonchondritic distribution of isotopes derived from short-lived
167 radioactive isotopes (Boyet and Carlson 2005, 2006; O'Neil et al. 2008; Brown et al. 2014).
168 Subsequently, gravitationally unstable cumulates of mantle silicate minerals may have

169 overturned to form more stable layered configurations that were resistant to the onset of large-
170 scale thermal convection (Elkins-Tanton 2008, 2012; Schaefer and Elkins-Tanton 2018).

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

180

181 EARTH'S EARLIEST CRUSTAL MINERALOGY

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

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

194 (1) Most near-surface primary mineralization was the consequence of widespread volcanic
195 activity and associated intrusive rocks.

196 (2) A significant fraction of Earth's surface (far more than today's world) was covered by a
197 globe-spanning water ocean prior to 4.37 Ga.

198 (3) Some volcanic terrains breached the ocean surface, resulting in significant areas of dry
199 land (though far less than today's world).

200 (4) A dynamic atmosphere rich in CO₂ and H₂O featured rain, lightning, and other surface
201 interactions.

202 The resulting hypothetical inventory of 262 early Hadean minerals ([Supplementary Table 1 and](#)
203 [associated Read-Me file](#)) is based on two principal criteria. First, we look to asteroidal
204 mineralogy preserved in stony achondrite meteorites, which provide an informative baseline.
205 Primary mafic and ultramafic igneous minerals and their thermal, aqueous, and shock alteration
206 products in achondrites point to 114 likely early Hadean minerals in Earth's crust (Morrison and
207 Hazen 2021; Hazen and Morrison 2021, 2022).

208 Of the 262 minerals that we propose formed on the Hadean Earth, 148 mineral species are not
209 yet known from meteorites. These phases were plausibly formed by dynamic processes in
210 Earth's shallow crust, hydrosphere, and atmosphere. We list more than 60 minerals, including 39
211 not yet found in meteorites, that were associated with volcanoes by condensation at fumaroles,
212 precipitation in zeolite-bearing basalt cavities, and thermal alteration in lava-borne xenoliths. We
213 speculate that aqueous alteration in Earth's shallow crust produced 106 minerals (at least 67 of
214 which have not been identified in meteorites) in hydrothermal veins, at marine and terrestrial

215 hydrothermal vents and geysers, in zones of serpentinization, and by low-temperature alteration.
216 An additional 110 species (44 appearing for the first time) may have arisen from processes on the
217 terrestrial surface, including authigenesis, freezing of aqueous solutions, impacts, lightning,
218 evaporation, and photo-reactions with sunlight (Table 1).

219 It is important to note a large number of possible early Hadean minerals that we do not
220 include in this speculative inventory. For example, we do not list mineral species that are (1) not
221 yet known from achondrite meteorites *and* (2) that are relatively rare on Earth today (i.e.,
222 minerals known from fewer than 20 localities; <https://mindat.org>, accessed 6 September 2021).
223 The gyrolite group of phyllosilicates, none of which is known from meteorites, is a case in point.
224 Gyrolite $[\text{NaCa}_{16}\text{Si}_{23}\text{AlO}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}]$ is found in association with basalt-hosted zeolite
225 minerals or hydrothermally altered lithologies in more than 100 localities (<https://mindat.org>,
226 accessed 16 September 2021) and therefore it is included in our inventory. However, other less
227 common members of the gyrolite group with similar compositions and parageneses, including
228 reyerite $[(\text{Na},\text{K})_2\text{Ca}_{14}(\text{Si},\text{Al})_{24}\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}]$, truscottite $[(\text{Ca},\text{Mn})_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot 2\text{H}_2\text{O}]$,
229 and tungusite $[\text{Ca}_4\text{Fe}_2\text{Si}_6\text{O}_{15}(\text{OH})_6]$, are known from fewer than 10 localities and are not
230 included. In addition, our list of the earliest Hadean minerals does not include species with a
231 number of rare elements, including Li, Be, B, Ga, Ge, Se, Rb, Sr, Y, Cd, Tl, Pb, and U. These
232 criteria reflect the relatively restricted physical and/or chemical conditions of formation that are
233 typical of many rare mineral species (Hazen and Ausubel 2016)—conditions we suggest that
234 were not present on Earth prior to 4.37 Ga.

235 We do not include minerals known exclusively or primarily from exotic achondrite lithologies
236 (Hazen and Morrison 2021; Morrison and Hazen 2021; Rubin and Ma 2021), including highly

237 reduced phases in enstatite chondrites [e.g., daubréelite (FeCr_2S_4); oldhamite (CaS); wasonite
238 (WS)]; rare phosphates and other minerals found as meteorite phases exclusively in angrites
239 [e.g., celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$); kirschsteinite (CaFeSiO_4); kuratite ($\text{Ca}_2\text{Fe}_5\text{TiO}_2\text{Si}_4\text{Al}_2\text{O}_{18}$);
240 matyhite [$\text{Ca}_9(\text{Ca}_{0.5}\square_{0.5})\text{Fe}(\text{PO}_4)_7$]; tsangpoite [$\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$]; or achondrite phases found
241 only in urelites [eskolaite (Cr_2O_3); suessite (Fe_3Si)]. Similarly, we omit rare minerals in silicate
242 inclusions in iron meteorites [armalcolite [$(\text{Mg,Fe})\text{Ti}_2\text{O}_5$]; kaersutite
243 ($\text{NaCa}_2\text{Mg}_3\text{AlTiSi}_6\text{Al}_2\text{O}_{24}$); yagiite ($\text{NaMg}_2\text{AlMg}_2\text{Si}_{12}\text{O}_{30}$)]; phases known only as alteration
244 products of calcium-aluminum inclusions [goldmanite ($\text{Ca}_3\text{V}_2\text{SiAl}_2\text{O}_{12}$); hutcheonite
245 ($\text{Ca}_3\text{Ti}_2\text{SiAl}_2\text{O}_{12}$)]; or any of more than a dozen rare oxides and silicates known only from the
246 Allende CV chondrite [Hazen and Morrison 2021; Rubin and Ma 2021; e.g., adrianite
247 ($\text{Ca}_{12}\text{Al}_4\text{Mg}_3\text{Si}_7\text{O}_{32}\text{Cl}_6$); beckettite ($\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$); chihuahuaite [$(\text{Fe,Mg})\text{Al}_{12}\text{O}_{19}$];
248 coulsonite [$(\text{Fe,Mg})\text{V}_2\text{O}_4$], wadalite ($\text{Ca}_6\text{Al}_5\text{Si}_2\text{O}_{16}\text{Cl}_3$)].

249 With the exception of 14 plausible sanidinite facies minerals found in thermally
250 metamorphosed xenoliths of mafic and ultramafic lithologies, we do not include metamorphic
251 minerals, such as those known exclusively from regional metamorphic or skarn/contact
252 metamorphic deposits. Thus, for example, minerals of the aenigmatite, osumillite, pumpellyite,
253 scapolite, or vesuvianite groups are not represented in our earliest terrestrial inventory. Such
254 phases require the formation of parent lithologies, then burial (in some instances by subduction)
255 and alteration of those rocks, and subsequent uplift and near-surface exposure (Philpotts and
256 Ague 2009; Brown 2013). While it is plausible that such mineral-forming sequences occurred

257 early in Earth's history, we defer listing most metamorphic minerals until later in the
258 Precambrian, when the advent of significant continental formation and orogenesis related to plate
259 tectonics enriched mineral inventories. Of special note in this regard, although localized
260 carbonate minerals likely formed in modest volumes at hot springs and in association with the
261 carbonation of mafic minerals exposed to the early CO₂-rich atmosphere, we do not list the more
262 than 350 minerals associated with contact metamorphism of carbonates and associated skarn
263 deposits (Hazen and Morrison 2022; their Supplementary Table 1).

264 A distinctive characteristic of Earth's crustal evolution has been the emplacement of highly-
265 evolved igneous lithologies that likely represent multiple stages of crystallization, partial
266 melting, and fractionation. Among these rock types are carbonate-bearing kimberlites and
267 carbonatites; complex granite pegmatites, noteworthy for minerals of rare elements such as B,
268 Be, Li, and REE; peraluminous igneous rocks; and Si-depleted alkali igneous suites (agpaitic
269 lithologies) that are exceptionally enriched in Na and K, with corresponding development of
270 feldspathoid minerals (Johannsen 1932, 1937; London 2008; Philpotts and Ague 2009; Bea et al.
271 2013; Furnes and Dilek 2017; Marks and Markl 2017; Ackerson et al. 2021). We suggest that the
272 diverse mineral species unique to these distinctive igneous rocks did not first appear until later in
273 the Hadean Eon (Hazen and Morrison 2022). Therefore, they will be considered in a subsequent
274 contribution.

275 We identify 262 kinds of minerals that plausibly formed within a few tens of millions of years
276 after the Moon-forming event (Supplementary Table 1; see also Supplementary "Read Me" file).
277 Of these minerals, 236 are valid species with names approved by the IMA-CNMNC. However,
278 in 26 instances we employ names that deviate from IMA conventions (indicated by blue
279 highlights in Supplementary Table 1). Four of these of these unapproved minerals, including

280 silica glass, basaltic glass, impact-produced amorphous CaSiO_3 , and maskelynite (impact
281 plagioclase glass), are non-crystalline phases, while two are as yet poorly characterized and
282 unnamed impact Mg-Fe silicates known only from meteorites (Ma et al. 2019a, 2019b), but
283 likely also present on the perpetually blasted early Hadean surface.

284 In 18 cases we lump two or more closely-related minerals into one mineral “root kind”
285 (Hazen et al. 2022). In some cases, we employ unapproved names for petrologically familiar
286 solid solutions. “Biotite” includes various Fe-bearing dark micas with the general formula
287 $[\text{K}(\text{Mg},\text{Fe}^{2+})_{3-x}\text{Al}_x(\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_{10}(\text{OH})_2)]$ (Fleet 2003; his Figure 172). “Chlorite” refers to all
288 Mg-Fe-Al-dominant members of the chlorite group, most commonly clinochlore
289 $[\text{Mg}_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8]$, but possibly extending to chamosite
290 $[(\text{Fe}^{2+},\text{Mg},\text{Al},\text{Fe}^{3+})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH},\text{O})_8]$ and sudoite $[\text{Mg}_2\text{Al}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8]$ in some
291 Hadean settings, as well (Deer et al. 2009). We lump greenalite $[(\text{Fe}^{2+},\text{Fe}^{3+})_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4]$
292 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
293 serpentine group minerals and they appear to form a continuous solid solution.

294 “Hornblende” encompasses a range of aluminous calcic clinoamphiboles, including members
295 of the tschermakite, hastingsite, and pargasite groups with general formula
296 $[(\square,\text{Na})\text{Ca}_2(\text{Mg},\text{Fe}^{2+})(\text{Al},\text{Si})_2\text{Si}_6\text{O}_{22}(\text{OH},\text{O})_2]$ (Deer et al. 1997; their Figure 279). “Melilite”
297 refers to intermediate members of the akermanite $[\text{Ca}_2\text{MgSi}_2\text{O}_7]$ -gehlenite $[\text{Ca}_2\text{Al}_2\text{SiO}_7]$ series
298 (Deer et al. 1986; their Figure 137); “plagioclase” denotes intermediate members of the albite
299 $(\text{NaAlSi}_3\text{O}_8)$ -anorthite $(\text{CaAl}_2\text{Si}_2\text{O}_8)$ series (Deer et al. 2001; their Figure 1); and we recognize

300 the intimate exsolution of K- and Na-rich alkali feldspars as “perthite.” We lump fluorapatite,
301 chlorapatite, and hydroxylapatite into “apatite” $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})]$; monazite-(Ce), monazite-
302 (La), monazite-(Nd), and monazite-(Sm) into “monazite” $[(\text{REE})(\text{PO}_4)]$; and allanite-(Ce),
303 allanite-(La), allanite-(Nd), and allanite-(Y) into “allanite”
304 $[\text{Ca}(\text{Y},\text{REE})\text{Ce}(\text{Al}_2\text{Fe}^{2+})(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})]$. Similarly, we use root names for nine zeolite
305 mineral groups: chabazite, clinoptilite, erionite, faujasite, ferrierite, heulandite, levyne,
306 phillipsite, and stilbite (Deer et al. 2004). Finally, in our system we use “orthoestatite” rather
307 than “enstatite” in order to make a clear distinction from clinoenstatite (all of which are
308 MgSiO_3).

309

310 **MINERALOGY OF THE EARLY HADEAN EON (> 4.37 GA): PRIMARY IGNEOUS PHASES**

311 In the following sections we consider 18 terrestrial formational environments for 262
312 plausible early Hadean minerals (Table 1; Supplementary Table 1). In each subsection, the
313 numbers and 3-letter acronyms in parentheses correspond to the 18 numbered rows in Table 1,
314 where they appear in the same order.

315

316 *1. Ultramafic Rocks (UMA):* The initial upper mantle lithologies of Earth’s crystallizing magma
317 ocean were ultramafic rocks, defined as igneous rocks composed predominantly of mafic
318 minerals and lacking significant feldspars or feldspathoids (Johannsen 1938; Dick 1989; Isley
319 and Abbott 1999; Guilbert and Park 2007; Philpotts and Ague 2009; Lambart et al. 2016).
320 Intrusive ultramafic rocks include olivine-dominant peridotite and pyroxene-dominant
321 pyroxenite, which are the two major lithologies of Earth’s upper mantle. In addition, komatiite is

322 an Mg-rich ultramafic volcanic rock with a distinctive quench texture of skeletal “spinfex”
323 olivine, clinopyroxene, orthopyroxene, and glass – features that point to olivine as a rapidly
324 crystallized liquidus mineral and thus suggesting a high temperature of eruption (> 1650 °C),
325 presumably when Earth had a much steeper geothermal gradient than today (Green 1975; Shore
326 and Fowler 1999; Faure et al. 2006).

327 Ultramafic lithologies played a significant role in the mineralogy of Hadean Earth’s upper
328 mantle (Rollinson 2007; Van Kranendonk et al. 2007), though significant uncertainty remains
329 regarding the relative volumes of ultramafic versus mafic rocks (e.g., Korenaga 2021). Dense
330 ultramafic rocks would not have accumulated at Earth’s early Hadean surface in any significant
331 volumes. However, entrained xenolithic rock fragments might have been a pervasive feature of
332 the Hadean crust. Therefore, 41 primary ultramafic minerals are included in our inventory
333 (Supplementary Table 1; column UMA).

334 The most common primary minerals in ultramafic rocks (Johannsen 1938) include forsteritic
335 olivine (Mg_2SiO_4); clinopyroxene, usually Mg-rich augite, but also aegirine-augite and diopside
336 [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
337 member, enstatite); chromite ($\text{Fe}^{2+}\text{Cr}_2\text{O}_4$); magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$); spinel (ideally MgAl_2O_4 ,
338 but often Cr-rich); ilmenite ($\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$); and apatite. Accessory phases (Johannsen 1938)
339 include calcic plagioclase; alkali feldspars [albite ($\text{NaAlSi}_3\text{O}_8$) and orthoclase (KAlSi_3O_8)];
340 feldspathoids, most commonly nepheline (NaAlSiO_4)]; zircon (ZrSiO_4); perovskite (CaTiO_3);
341 rutile (TiO_2); titanite (CaTiSiO_5); pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$); and analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$).
342 Sulfides, including pyrite, pyrrhotite (Fe_7S_8), and pentlandite [$(\text{Ni}, \text{Fe})_9\text{S}_8$], often associated with

343 platinum group elements (PGE), are also common accessory minerals in ultramafic rocks,
344 perhaps at times derived from an immiscible S- and PGE-rich fluid (e.g., Maier 2005; Collins et
345 al. 2012). In magmas with significant water content, hydrous biopyriboles such as hornblende,
346 biotite, and phlogopite [$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] may be primary phases, as well. Note that Hazen
347 and Morrison (2022) catalogued 123 mineral species that have been identified in a variety of
348 Precambrian ultramafic intrusive and extrusive igneous rocks, including some hydrothermally
349 altered phases and associated polymetallic deposits. We suggest that most of those species
350 incorporate rare elements and probably would not have appeared until significantly later in
351 Earth's history.

352

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

364 Of the several varieties of mafic rocks found on Earth today, only tholeiitic basalts associated
365 with partial melting of depleted mantle lithosphere by mantle plumes are likely to have played a

366 major role in the early Hadean Eon (e.g., Sharkov and Bogina 2009). By contrast, other mafic
367 lithologies, including alkali basalts and boninities, represent later (though possibly Hadean)
368 partial melts. For example, boninitic magmas, which are relatively enriched in Si and Mg, have
369 been ascribed to a two-stage melting process associated with subduction and are thus of later
370 genesis (Duncan and Green, 1987).

371 Hazen and Morrison (2022) identified 93 mineral species documented to occur in
372 Precambrian mafic igneous rocks. However, most of those minerals are scarce phases that
373 incorporate one or more rare elements and therefore probably appeared later in the Precambrian.
374 Here we tabulate 39 primary minerals (Supplementary Table 1; column MAF) that likely
375 occurred prior to 4.37 Ga in basalt and gabbro, including calcic plagioclase (usually labradorite
376 or bytownite), clinopyroxene (dominantly augite, but also diopside), orthopyroxene (ranging
377 from Mg-rich enstatite to more Fe-rich bronzite or hypersthene), forsteritic olivine, hornblende,
378 biotite, apatite, magnetite, ilmenite, spinel, and chromite (Johannsen 1937). If present, quartz
379 (SiO_2) and orthoclase were among the last minerals to crystallize. Accessory phases include
380 zircon, pyrope, corundum (Al_2O_3), titanite, and graphite (C), as well as Fe sulfides (pyrite and
381 pyrrhotite). Among the most important solid phases associated with mafic volcanism is basaltic
382 glass. Though not an approved mineral species by the IMA-CNMNC, we recognize basaltic
383 glass as a “mineral natural kind” (Supplementary Table 1).

384

385 *3. Silica-rich rocks (SIL):* An important unanswered question is the age and extent of Earth’s
386 earliest Si-rich (i.e., granitic/felsic) lithologies. So-called “TTG” (tonalite–trondhjemite–
387 granodiorite) rocks with quartz and Na-Ca feldspar (though relatively minor K-feldspar), often in
388 association with greenstone belts, represent the dominant lithologies preserved from the

389 Eoarchean Era (Condie and Benn 2006; Hamilton 2007; O’Neil et al. 2011; O’Neill and Debaille
390 2014). The origin of these TTG terranes has been ascribed to partial melting of subducted
391 oceanic basalt crust – a process that would have been enhanced by the elevated early
392 Precambrian geothermal gradient (Martin and Moyen 2002; Martin et al. 2005; Hamilton 2007).
393 However, subduction (and the implication of related plate tectonic processes) is not required for
394 TTG formation. Similar partial melting events could have occurred long before modern-style
395 subduction by the chaotic foundering and subsequent melting of mafic crust (e.g., Hamilton
396 2007) or by impact melting (Grieve et al. 2006). Consequently, we suggest that Si-rich
397 lithologies, including TTG suites and other quartz-normative rocks, would have been an early
398 and pervasive feature of Earth’s Hadean crust.

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

409 Additional evidence for early Si-rich igneous lithologies comes from the Moon and asteroids.
410 On the Moon, localized Si-rich volcanic terrains appear to represent episodes of basalt partial
411 melting, perhaps related to impact melting (Chevrel et al. 1999; Jolliff et al. 2006, 2011). Similar

412 mineralogical outliers have been associated with the partial melting of planetesimals of
413 carbonaceous and ordinary chondrite compositions, for example by Collinet and Grove (2020),
414 who conducted partial melting experiments on various chondritic meteorites. Taking extra care
415 to retain critical volatile alkali elements, they produced initial (up to ~15 wt %) low-density,
416 high-viscosity melts enriched in silica, alumina, and alkalis. Those experimental results parallel
417 the discovery of rare andesitic meteorites – among the oldest known achondrite meteorites at
418 ~4.565 Ga – that presumably represent primitive igneous planetesimal crusts formed prior to
419 significant alkali loss (Barrat et al. 2021). Such rare andesitic meteorites are interpreted as
420 fragments of thin planetesimal crusts that overlaid the volumetrically dominant mafic mantle
421 lithologies, which compose the vast majority of achondrite meteorites.

422 Analogous minor volumes of highly fractionated, localized melts must have played a role in
423 the near-surface mineralogical diversification of early Earth (Warren 1989; Hickman and
424 VanKranendonk 2012; Carlson et al. 2019). The “Bowen trend” of Si-rich residues (Bowen
425 1928) led to Si-, Al-, and alkali-enriched magmas via 2 to 3% melting of wet peridotitic mantle,
426 which is depleted in alkalis relative to primitive chondrites (Kinzler and Grove 1992; Baker et al.
427 1995). In addition, Miyazaki and Korenaga (2019a, 2019b) suggest that fractional crystallization
428 of a magma ocean resulted in outer layers with mafic minerals relatively enriched in Fe (i.e., the
429 “Fenner fractionation trend;” Fenner 1929). Harrison (2009) amplifies this theme by positing a
430 relatively shallow magma ocean (< 250 km) with forsterite crystallization and settling. The
431 residual Si- and Al-rich melt rises to crustal depths and rapidly nucleates feldspar (Morse 1986),
432 creating a tonalitic, high-viscosity mush that coalesced into “rockbergs of stable, felsic crust.”
433 Harrison (2009) suggests that tonalitic crust could have appeared shortly after Earth’s formation,

434 as well as soon after the Moon-forming event – hypotheses consistent with evidence from
435 Hadean zircons (Harrison et al. 2008).

436 The primary mineralogy of early Hadean quartz normative rocks would have included quartz,
437 plagioclase (typically Na-dominant oligoclase-andesine), orthoclase, microcline (KAlSi_3O_8),
438 perthite, muscovite [$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$], biotite, hornblende, arfvedsonite
439 [$\text{NaNa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$], anthophyllite [$\square\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$], almandine
440 ($\text{Fe}^{2+}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), orthopyroxene (usually an intermediate Mg-Fe composition, such as
441 hypersthene), clinopyroxene (including augite, diopside, and aegirine-augite), fayalite (Fe_2SiO_4),
442 titanite, magnetite, apatite, zircon, rutile, ilmenite, pyrite, and pyrrhotite (e.g., Johannsen 1932).

443 In Supplementary Table 1 (column SIL) we tabulate 32 plausible minerals in early Hadean Si-
444 rich rocks. This list is admittedly conservative. For example, we do not list the most common
445 minerals with essential Li [spodumene ($\text{LiAlSi}_2\text{O}_6$) or Li-rich mica], Be (beryl group), or B
446 (tourmaline group), each of which requires significant local concentration of a rare element
447 (London 2008). Neither do we include such common granitic accessory minerals as cassiterite
448 (SnO_2), molybdenite (MoS_2), or topaz ($\text{Al}_2\text{SiO}_4\text{F}_2$)– phases that we suggest first appeared later
449 in the Hadean Eon, based in part on their absence in the Si-rich lithologies of known lunar or
450 meteoritic samples.

451

452 *4. Anorthosite (ANO):* Anorthosites are distinctive igneous rocks composed almost entirely of
453 macrocrystalline plagioclase feldspar. On Earth, most large anorthosite bodies formed during one
454 relatively short, enigmatic interval during the Mesoproterozoic, between ~1.45 to 1.10 Ga

455 (Philpotts and Ague 2009, and references therein). Other calcic ($An > 80$) megacrystic
456 anorthositic bodies occur as minor lithologies in some greenstone belts of the Archean Eon as
457 early as ~ 3.7 Ga (Ashwal 2010). However, recent speculations regarding the possibility of
458 extensive anorthosite bodies on early Earth – perhaps even continent-scale anorthositic
459 development, now lost to subduction (Kawai et al. 2009; Maruyama et al. 2013; Maruyama and
460 Ebisuzaki 2017; Dohm et al. 2018; Yoshiya et al. 2018) – deserve comment.

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

475 We conclude that plagioclase-dominant igneous rocks would have represented a minor
476 component of Earth's early crust. However, all of the primary minerals associated with
477 anorthosite today, including calcic plagioclase, alkali feldspar, clinopyroxene, orthopyroxene,

478 forsterite, hornblende, biotite, zircon, titanite, magnetite, ilmenite, rutile, garnet, and pyrite
479 (Johannsen 1937), are also present in the mineral inventories of other probable Hadean igneous
480 minerals (Supplementary Table 1; column ANO). Therefore, the presence or absence of
481 anorthosite does not significantly alter the conclusions of this compilation.

482

483 *5. Volcanic fumarole minerals (FUM):* In addition to the primary igneous minerals outlined
484 above, three other processes related to volcanism may have added to early Earth's mineral
485 diversity. Today, volcanic fumaroles and mariolitic cavities host a remarkable variety of more
486 than 400 minerals that condense directly from hot vapors (Grapes 2006; Vergasova and Filatov
487 2016; Hazen and Morrison 2022). Of these species, we ascribe only 23 fumarolic minerals that
488 incorporate relatively common elements to the earliest episodes of Hadean volcanism
489 (Supplementary Table 1; column FUM). Five of these phases are silicates [albite, cristobalite
490 (SiO_2), fluorophlogopite, sanidine (KAlSi_3O_8), and tridymite (SiO_2)], one is the halide fluorite
491 (CaF_2), two are native elements (iron and sulphur), and the remaining 10 are sulfides known to
492 be common in modern fumaroles with reduced S-rich vapors [bismuthinite (Bi_2S_3), chalcopyrite
493 (CuFeS_2), digenite ($\text{Cu}_{1.8}\text{S}$), galena (PbS), greenockite (CdS), marcasite (FeS_2), orpiment
494 (As_2S_3), pyrite, realgar (AsS), and wurtzite (ZnS)].

495

496 *6. Basalt-hosted zeolites and other vesicle-filling minerals (ZEO):* A prominent mineralogical
497 feature of many basaltic formations is the extensive development of zeolites and other minerals
498 that precipitated from warm to hot fluids in vesicles. More than 80 zeolite minerals, most of them
499 rare, have been identified (Deer et al. 2004; <https://rruff.info/ima>, accessed 6 September 2021).

500 We include 27 vesicle-deposited minerals, including 19 of the most common basalt-hosted
501 zeolite minerals or mineral groups (Supplementary Table 1; column ZEO). For example, we list
502 analcime, chabazite, faujasite, heulandite, laumontite, natrolite, phillipsite, stilbite, and
503 thompsonite, as possible early Hadean minerals. Other plausible ancient minerals deposited in
504 basalt cavities include aragonite and calcite (both CaCO_3), gyrolite, and prehnite
505 $[\text{Ca}_2\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$.

506

507 **MINERALOGICAL CONSEQUENCES OF THE EARLY ATMOSPHERE AND OCEANS**

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

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

523 According to some models, the post-lunar magma ocean was largely devolatilized, thus
524 transferring most H₂O, CO₂, alkali metals, and other volatile elements/molecules to the near-
525 surface environment (Zahnle et al. 2010). Even so, some water must have persisted in the mantle,
526 for example as H in nominally anhydrous minerals (Bell and Rossman 1992; Bolfan-Casanova
527 and Keppler 2000; Kohn and Grant 2006; Tikoo and Elkins-Tanton 2017). After the synestia,
528 additional volatiles would have been delivered to Earth's surface by a steady influx of asteroids
529 and comets (e.g., Albarède 2009; Alexander et al. 2012). However, the relative importance of
530 Earth's original volatile budget versus subsequent contributions through post-lunar bombardment
531 remains a matter of debate (Kasting and Howard 2006; Zahnle et al. 2010, 2020).

532 Widely cited models of the early atmosphere posit a dense mixture primarily of CO₂ and
533 H₂O, with N₂, H₂, CO, CH₄, and H₂S, perhaps with a surface pressure greater than 100
534 atmospheres (Zahnle et al. 2010; Pilchin and Eppelbaum 2012). An added wrinkle is speculation
535 that intense post-lunar bombardment of Earth by Fe-Ni metal-bearing inner solar system objects
536 might have generated a correspondingly reduced atmosphere enriched in H₂, CH₄, and NH₃, and
537 thus conducive to some models of organic chemical reactions as prelude to the origins of life
538 (Sekine et al. 2003; Zahnle et al. 2020). However, such alteration of the atmosphere by
539 bombardment may have significantly post-dated 4.37 Ga (Evans et al. 2018; Morbidelli et al.
540 2018). In any event, a dense early atmosphere would have led to consequential near-surface
541 feedbacks. For example, water can be very soluble in silicate magmas, which can affect
542 atmospheric composition by H₂O drawdown (Schaefer and Fegley 2010).

543 Similarly, atmospheric CO₂ readily reacts with mafic minerals to form carbonates, as
544 observed in modern-day ophiolite terrains (Sleep and Zahnle 2001; Kelemen and Matter 2008;
545 Streit et al. 2012; Chavagnac et al. 2013; Shibuya et al. 2013; Giampouras et al. 2020; Kadoya et
546 al. 2020). Incorporation of volatiles by near-surface rocks and magma, coupled with active
547 convection and overturn, could have significantly increased water contents of the crust and upper
548 mantle, ultimately leading to volcanic venting of volatiles rich in H, C, O, N, and S (Gaillard and
549 Scaillet 2014). Even though the initial surface environment of the cooling magma ocean was too
550 hot for the accumulation of liquid water, the primary igneous minerals outlined in sections above
551 would have been subject to alteration by interactions with steam and/or supercritical H₂O- and
552 CO₂-bearing fluids (Zahnle et al. 1988). Therefore, we adopt the view that Hadean Earth
553 developed an active hydrosphere, perhaps within a few million years following the synestia
554 (Wilde et al. 2001; Mojzsis et al. 2001; Harrison 2009; Elkins-Tanton 2011).

555 Many uncertainties remain regarding Earth's earliest water cycle. For example, the water
556 content of volcanic exhalations (and hence the rate of cycling through the mantle) may have been
557 strongly dependent on atmospheric pressure. Gaillard and Scaillet (2014) suggest that at surface
558 pressure \gg 1 atm, as is postulated for Earth soon after the Moon's formation, volcanic emissions
559 are N₂- and CO₂-rich, but relatively dry. By contrast, at \sim 1 atm volcanic gases are dominated by
560 H₂O, whereas surface pressures \ll 1 atm favor sulfur-rich gases. If Earth's earliest atmosphere
561 was in excess of 100 bars, then an active surface hydrological cycle may have been delayed.

562 Ultimately, surface cooling below 100 °C would have supported condensation of water,
563 resulting in a warm early ocean (Abe and Matsui 1988; Abe 1993; Schaefer and Fegley 2010;
564 Ernst et al. 2016). Models of early Hadean oceans suggest important differences from those of

565 today. For example, Hadean oceans were anoxic and thus likely enriched in soluble reduced ions
566 such as Fe^{2+} , Mn^{2+} , and Co^{2+} compared to today's oceans (Anbar and Knoll 2002; Anbar
567 2008). Dissolved carbon dioxide from a dense CO_2 -rich atmosphere may have resulted in
568 initially acidic conditions (Morse and Mackenzie 1998). Early Hadean oceans also probably had
569 significantly higher salinity than modern oceans, both because they were warmer and because
570 Earth's volatile elements (including alkali metals and halogens) were concentrated near the
571 surface after the synestia and before extensive formation of crustal minerals such as alkali
572 feldspars with Na and K (Holland 1984; Knauth 2005; Izawa et al. 2010; Zahnle et al. 2010;
573 Charnay et al. 2017; Marty et al. 2018).

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

582 We conclude that by 4.37 Ga, lakes and oceans may have covered a significant fraction of
583 Earth's surface (Wilde et al. 2001; Elkins-Tanton 2011; Dong et al. 2021), while the shallow
584 subsurface experienced significant hydrothermal circulation (Heinrich and Henley 1989; Pirajno
585 2009). In the following sections we consider more than 150 plausible minerals that may have
586 formed through fluid-rock interactions prior to 4.37 Ga.

587

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

598

599 8. *Terrestrial hot springs and geysers (HSG)*: The exposed volcanic surface of the Hadean world,
600 though possibly less extensive than today, would have featured abundant subaerial hot springs
601 and geysers that produced a range of geothermal minerals (Pirajno 2020), perhaps including the
602 earliest terrestrial occurrences of carbonates and sulfates [e.g., anhydrite (CaSO_4), aragonite,
603 baryte (BaSO_4), calcite, and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)]. Widespread low-temperature aqueous
604 alteration of Hadean lithologies would also have enriched early Earth's inventory of hydrous
605 silicates, including clay minerals and zeolites (Deer et al. 2004; Wilson 2013). Supplementary
606 Table 1 (column HSG) lists 30 postulated hot springs and geyser minerals that may have
607 precipitated prior to 4.37 Ga.

608

609 9. *Seafloor hydrothermal vents (SHT)*: Earth's earliest seafloor would have been punctuated by
610 numerous vents that emitted mineral-rich hydrothermal fluids, though the character of vent

611 chemistry and consequent mineralization may have differed significantly from today. We suspect
612 that compositions would have ranged, as they do today, from sulfide-dominated “black smokers”
613 to carbonate-bearing “white smokers” (Hekinian et al. 1980; Haymon and Kastner 1981;
614 Palandri and Reed 2004; Schwarzenbach and Steele-MacInnis 2020). Accordingly, we list a
615 subset of 32 relatively common minerals, primarily sulfides (19 species), as well as carbonates,
616 sulfates, and hydrous phases that likely occurred in seafloor hydrothermal vent systems
617 (Supplementary Table 1, column SHT).

618

619 *10. Lava-hosted xenolith minerals (XEN):* A modest number of early Hadean minerals were
620 likely formed as a consequence of high-temperature, low-pressure (sanidinite facies)
621 metamorphism of xenoliths, which are varied lithic fragments entrained in a magma (e.g., Grapes
622 2005). Hazen and Morrison (2022) catalogued 127 plausible Hadean xenolith minerals.
623 However, we suggest that only 14 oxide and silicate species would have been likely to form via
624 sanidinite facies metamorphism of early Hadean ultramafic, mafic, and TTG xenoliths
625 (Supplementary Table 1, column XEN). Furthermore, with the possible exceptions of
626 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
627 the igneous rocks already discussed. Note in particular that phases derived from Al-rich
628 sediments [corundum, mullite ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$; $x \sim 0.4$), sillimanite (Al_2SiO_5)] or by reaction
629 with carbonate xenoliths [gehlenite, larnite (Ca_2SiO_4), wollastonite (CaSiO_3)], which are
630 commonly found in recent sanidinite facies metamorphic rocks, are not included in our
631 inventory.

632

633 *11. Hadean serpentinization (SER):* The serpentinization of mafic and ultramafic rocks, by which
634 Fe- and Mg-bearing minerals are hydrated in low- to moderate-temperature (to ~400 °C), near-
635 surface aqueous environments, has been a significant mineral-forming process throughout Earth
636 history (Moody 1976; Russell et al. 2010; Shrenk et al. 2013; Shibuya et al. 2015; Lamadrid et
637 al. 2017; Korenaga 2021; Voosen 2021). Serpentinization played a major role in Earth's crustal
638 evolution by transforming ocean floor mafic and ultramafic rocks to assemblages of serpentine,
639 brucite, magnetite, and dozens of other phases (Blais and Aubrey 1990; Lowell and Rona 2002;
640 Palandri and Reed 2004; Shrenk et al. 2013; Holm et al. 2015; Yoshiya et al. 2018). In
641 Supplementary Table 1 (column SER) we list 46 minerals associated with serpentinization of the
642 primary minerals in near-surface Hadean mafic and ultramafic lithologies (see also Johannsen
643 1938 for lists of common secondary minerals in these rocks). Of these phases, 24 are hydrated
644 Mg-bearing minerals and 18 contain Fe and/or Ni.

645

646 *12. Low-temperature aqueous alteration (LTA):* In addition to the diverse minerals formed by
647 serpentinization and by precipitation associated with hydrothermal systems, submarine vents, hot
648 springs, and geysers, relatively low-temperature (< 100 °C) aqueous alteration of Hadean mafic
649 and ultramafic lithologies in subaerial and shallow subsurface environments may have produced
650 scores of mineral species, most notably hydroxides, zeolites, clay minerals, and other hydrous
651 silicates (Deer et al. 2004; Wilson 2013). In Supplementary Table 1 (column LTA) we catalog
652 67 plausible aqueous alteration phases from Earth's first 100 million years. Note that these
653 phases in part mirror minerals found in achondrite meteorites that have experienced aqueous
654 alteration – 22 species are common to both environments (Hazen and Morrison 2021a).

655

656 *13. Marine authigenic minerals (AUT):* Interactions of early Hadean seawater with serpentinized
657 rocks and seafloor sediments likely produced an assemblage of authigenic phases, defined as
658 minerals formed *in situ* as a consequence of direct precipitation from an aqueous solution, as
659 opposed to aqueous alteration of prior minerals (see above), for example as a carbonate cement
660 in detrital sediments. Following the conventions of Hazen and Morrison (2022), authigenesis
661 refers only to formation of minerals in low-*T* (< 100 °C) shallow sedimentary or porous near-
662 surface environments. We list 39 possible authigenic minerals (Supplementary Table 1; column
663 AUT), most of which are zeolites, clays, or other hydrous phases.

664

665 *14. Minerals formed by freezing (ICE):* The timing of Earth's earliest polar ice caps is unknown,
666 but localized episodes of freezing may have occurred, especially if Earth's axial inclination was
667 episodically greater than today. If so, then as many as three additional mineral species - ice
668 (H₂O), hydrohalite (NaCl·2H₂O), and ikaite (CaCO₃·6H₂O) – may have occurred in cold regions
669 (Aquino et al. 2021; Supplementary Table 1; column ICE).

670

671

OTHER MINERAL-FORMING PROCESSES

672 At least four additional subaerial processes – impacts, lightning, evaporite formation, and
673 photo-oxidation – may have added to early Earth's mineral diversity.

674

675 *15. Impact mineralization (IMP):* Impact mineralization would have been a pervasive feature of
676 the Hadean landscape (e.g., Koeberl 2006). Marchi et al. (2014) proposed a bombardment model
677 of early Earth that suggests repeated reprocessing of most of Earth's surface by large impacts

678 prior to 4 Ga. They posit, “No substantial large region of the Earth’s surface could have survived
679 untouched by impacts and associated outcomes.”

680 Meteorites and terrestrial rocks record shock events with peak transient temperatures and
681 pressures that may have exceeded 3,000 °C and 100 GPa lasting several seconds (Ohtani et al.
682 2004; Xie et al. 2006; Tomioka and Miyahara 2017; Stöffler et al 2018, their tables 4 through
683 11). The mineralogical consequences of such violent events on ultramafic, mafic, and TTG
684 lithologies are well documented through studies of dozens of shocked phases in meteorites and
685 from terrestrial impact craters (Koeberl 2002; Tomioka and Miyahara 2017; Ma 2018; Stöffler et
686 al. 2018; Tschauner 2019; Rubin and Ma 2021). Morrison and Hazen (2021; their Table 2)
687 documented 40 impact minerals known from a range of meteorites. In Supplementary Table 1
688 (column IMP) we include 41 minerals, of which 36 are also in our inventory of meteorite
689 minerals. Five proposed early Hadean terrestrial impact minerals are not yet known from
690 meteorites: akaogiite (TiO_2 ; El Goresy et al. 2010), maohokite (MgFe_2O_4 ; Chen et al. 2019),
691 reidite (ZrSiO_4 ; Glass et al. 2002), reSITE (TiO_2 ; Tschauner et al. 2020), and yoshiokaite [Ca_{1-x}
692 $(\text{Al,Si})_2\text{O}_4$; Vaniman and Bish 1990]. We do not include impact-generated martensite (α -Fe,Ni)
693 and allabogdanite [$(\text{Fe,Ni})_2\text{P}$], as they arise exclusively in iron meteorites. Note also that in 5
694 instances [akimotoite—hemleyite, $(\text{Mg,Fe})\text{SiO}_3$; bridgmanite—hiroseite, $(\text{Mg,Fe})\text{SiO}_3$;
695 periclase—wüstite or “magnesiowüstite,” $(\text{Mg,Fe})\text{O}$]; ringwoodite—ahrensite, $(\text{Mg,Fe})_2\text{SiO}_4$;
696 and wadsleyite—asimowite, $(\text{Mg,Fe})_2\text{SiO}_4$] we lump pairs of isostructural species with Mg and
697 Fe end-members because observed shock phases are typically of intermediate compositions
698 (Morrison and Hazen 2021; Hazen et al. 2022).

699 Many of these impact phases are dense high-pressure polymorphs of abundant rock-forming
700 minerals, including olivine, pyroxene, feldspar, and spinel group oxides. The list also includes
701 two shock-induced amorphous phases, silica glass (SiO₂) and the impact plagioclase glass
702 known as maskelynite.

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

707

708 *16. Lightning minerals (LIG):* Lightning, which appears to be a pervasive attribute of both
709 terrestrial and gaseous planets with turbulent atmospheres (Williams and Krider 1983; Russell et
710 al. 2008, 2011; Lorenz 2018), is an intriguing and as yet little studied mineral-forming
711 mechanism. In this context, lightning is best known for forming hollow branching structures of
712 fused sediments called fulgurites (Essene and Fisher 1986; Grapes 2006; Pasek et al. 2012).
713 These fascinating objects hold a modest inventory of 9 reported mineral species (Hazen and
714 Morrison 2022), including such reduced phases as graphite, silicon (Si), moissanite (SiC), and
715 schreibersite (Fe₃P). However, we suspect that additional reduced lightning-generated minerals
716 may be associated with strikes on ultramafic and mafic lithologies, notably in association with
717 volcanic lightning (McNutt and Williams 2009; Cimarelli et al. 2014; Van Eaton et al. 2016;
718 Cartier 2020; Smith et al. 2021). Such occurrences may incorporate mineralogical novelties
719 (silicides, phosphides, metal alloys), which may be difficult to detect and recover. For example,
720 the highly-reducing environment generated by the influx of electrons from a lightning strike has
721 been invoked as a possible source of prebiotic reduced P compounds (Pasek and Block 2009;

722 Feng et al. 2021; Hess et al. 2021). Similarly, Ballhaus et al. (2017, 2018a, 2018b, 2021) suggest
723 that enigmatic ultra-reduced phases in ophiolites, including moissanite and a variety of native
724 elements and alloys (e.g., Al, Fe, and Si) may result from lightning strikes, in contrast to Griffin
725 et al. (2016, 2017) and Yang et al. (2018), who argue for a deep-mantle origin of these reduced
726 phases. Similar arguments could be extended to Hadean lightning, especially strikes associated
727 with active volcanoes, and its effects on mafic/ultramafic rocks. Therefore, we list 12 plausible
728 early Hadean lightning-generated minerals (Supplementary Table 1; column LIG).

729

730 *17. Evaporites (EVA):* Evaporite mineralization was an inevitable consequence of land
731 surrounded by a saline ocean. Hazen and Morrison (2022) catalog 210 prebiotic evaporite
732 minerals; however, the great majority of those species are rare borates, halides, sulphates, or
733 carbonates that only appear as a consequence of the evaporation of large stranded saline water
734 bodies or brines after continent-scale landmasses appeared (Holser 1979; Boggs 2006). We list
735 14 plausible early Hadean evaporate minerals, including halides [halite (NaCl); sylvite (KCl);
736 and carnalite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$)], sulphates [anhydrite; gypsum; kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$);
737 langbeinite ($\text{K}_2\text{Mg}_2(\text{SO}_4)_3$); kainite ($\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$); and polyhalite
738 ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$)], and carbonates [calcite; magnesite (MgCO_3)], as recorded in
739 Supplementary Table 1 (see column EVA).

740

741 *18. Minerals formed by photo-reactions (PHO):* A handful of new minerals may have been
742 formed through the effects of sunlight on prior minerals (Kim et al. 2013; Hazen and Morrison
743 2022). For example, pararealgar (As_4S_4) is a common photo-reaction byproduct of realgar,

744 which was a likely early Hadean fumarolic mineral (Roberts et al. 1980). Of special interest are
745 photo-oxidation reactions of reduced Fe^{2+} , Mn^{2+} , and Cu^{1+} minerals, which may have produced
746 Fe^{3+} -, Mn^{3+} -, Mn^{4+} -, and Cu^{2+} -bearing minerals long before the biologically-mediated global
747 oxygenation of the Neoproterozoic Era. For example, Kim et al. (2013) demonstrated that siderite
748 (FeCO_3) in water breaks down to ferric iron oxides [magnetite (Fe_3O_4) or maghemite
749 ($\text{Fe}_{2.67}\text{O}_4$)] plus H_2 when exposed to ultraviolet light. Similarly, ramsdellite (MnO_2) and
750 digenite ($\text{Cu}_{1.8}\text{S}$) are possible products of photo-oxidation. In Supplementary Table 1 (column
751 PHO) we list 5 minerals that might have appeared through the action of sunlight on prior species.

752

753

IMPLICATIONS

754 *Early Hadean mineralogical parsimony*: This contribution lists 262 minerals that may have
755 emerged on Earth prior to 4.37 Ga via one or more of 18 formation processes. The total of 534
756 combinations of a mineral with a formation process tabulated in Supplementary Table 1
757 represents only 5% of the 10,556 combinations of 5659 mineral species formed by 57 processes
758 recorded by Hazen and Morrison (2022) for Earth today. At least 294 meteorite species, formed
759 by 13 pre-terrestrial processes as detailed in Parts I through V of this series, contributed an
760 additional 455 mineral/formation combinations that would have been present at or near Earth's
761 surface continuously since crustal solidification (Supplementary Table 1). Nevertheless, the
762 diversity of Earth's mineral kingdom has expanded by an order of magnitude since the early
763 Hadean Eon as enhanced fluid-rock interactions, plate tectonics, and biological influences have
764 come into play.

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

772 Interestingly, the formation mechanisms of minerals that we ascribe to early Earth may
773 closely parallel those of Mars during its first billion years. Like Earth, Mars probably
774 experienced an early magma ocean with subsequent wide-ranging mafic volcanism, as well as
775 minor volumes of Si-, Al-, and alkali-rich partial melts. Mars had a dynamic and extensive
776 hydrosphere, with associated mineralization by hydrothermal deposition, water-rock alteration,
777 authigenesis, and evaporites. And, like Earth, the surface of early Mars was subject to impact
778 mineralization, photo-oxidation, lightning, and freezing, with the addition of the full spectrum of
779 meteorite minerals. Consequently, we suggest that Part VI of the evolutionary system of Earth's
780 mineralogy may provide a baseline for Mars mineralogy, as well.

781

782 *Mineral network analysis:* Network graphs have the potential to reveal relationships among large
783 numbers of minerals and their modes of formation (Morrison et al. 2017). The earliest stages of
784 Earth's mineral evolution are illustrated in [Figure 1](#), which is a bipartite network graph that
785 illustrates relationships among 442 terrestrial and/or meteorite minerals and 31 processes by
786 which those minerals formed. This representation of minerals that would have been found on
787 Earth prior to 4.37 Ga includes 13 mineral-forming processes in meteorites (represented by black

788 icons shaped as a star, disk, cloud, or planet) and 18 mineral-forming processes on early Earth
789 (represented by black icons shaped as a volcano, droplet, planet, lightning, or lightbulb). Mineral
790 nodes appear in three colors: red for 180 meteorite minerals not expected to form on early Earth,
791 green for 148 minerals suspected to form on early Earth but not known from meteorites, and
792 yellow for 114 minerals from both groups.



793

794 Figure 1. This bipartite network graph illustrates relationships among 442 different mineral
795 species (represented by square- or diamond-shaped colored nodes) and 31 formation processes of
796 those minerals (represented by various shaped black nodes). The gray lines (“edges”) between

797 these two types of nodes indicate 988 proposed combinations of a mineral species and a mode of
798 formation. Note that each mineral is linked to one or more mode of formation, while each mode
799 of formation is linked to one or more minerals.

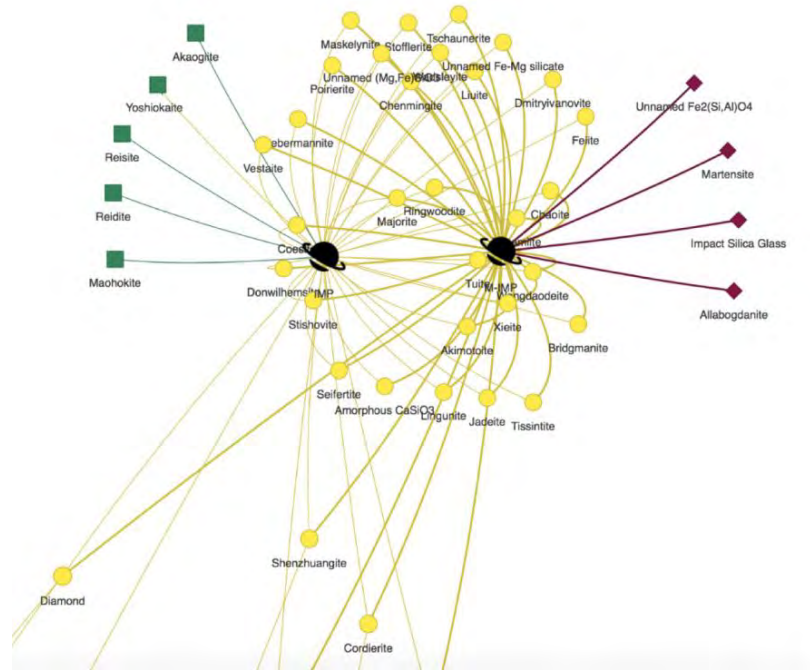
800 This network graph includes 13 nodes representing formation processes associated with
801 meteorites and 18 nodes representing formation processes occurring on early Earth. The 442
802 minerals include 148 species from early Earth only, represented by green squares; 180 species
803 from meteorites only, represented by red diamonds; and 114 species from both meteorites and
804 early Earth, represented by yellow circles. See Figures 2A through 2D for detailed enlargements
805 of four areas of this graph.

806

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

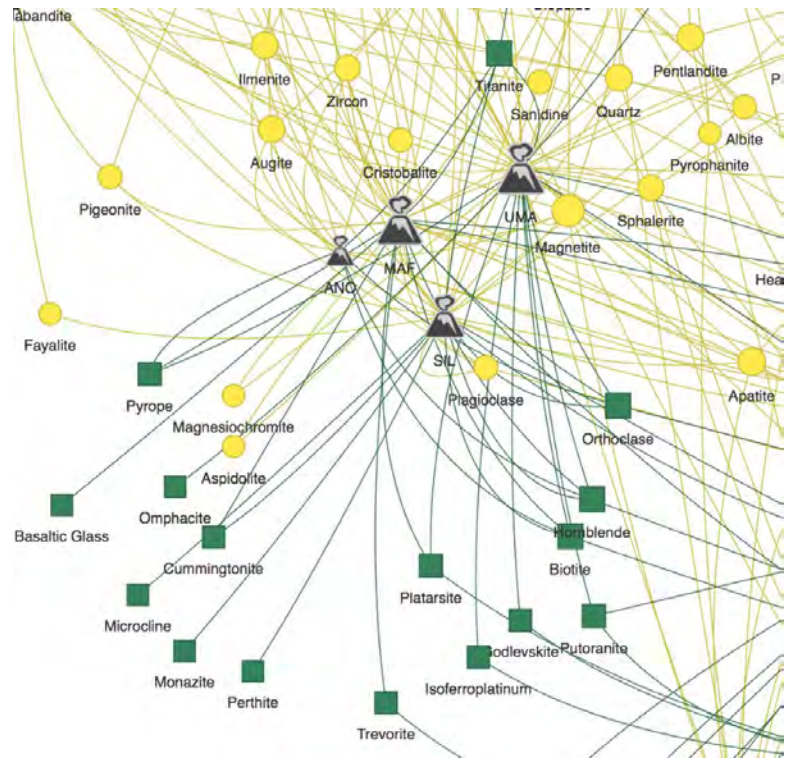
812 **Figure 2** focuses on key areas of this network graph. As might be expected, significant
813 overlaps between terrestrial and meteorite minerals occur among some of these various subsets
814 of early Hadean mineralogy. For example, 36 of 41 impact-generated minerals suspected to have
815 occurred on early Earth are also found in meteorites (**Figure 2A**). Most of these phases are
816 unique to the extremely high-temperature and high-pressure conditions of shock metamorphism.
817 Therefore, nodes representing meteorite and terrestrial impact formation processes lie close to
818 each other at the top of the graph, but significantly separated from most other minerals. Indeed,

819 only five minerals, including diamond (as a stellar condensate), clinoenstatite, and cordierite (in
820 xenoliths), connect impact minerals with other early Earth minerals.



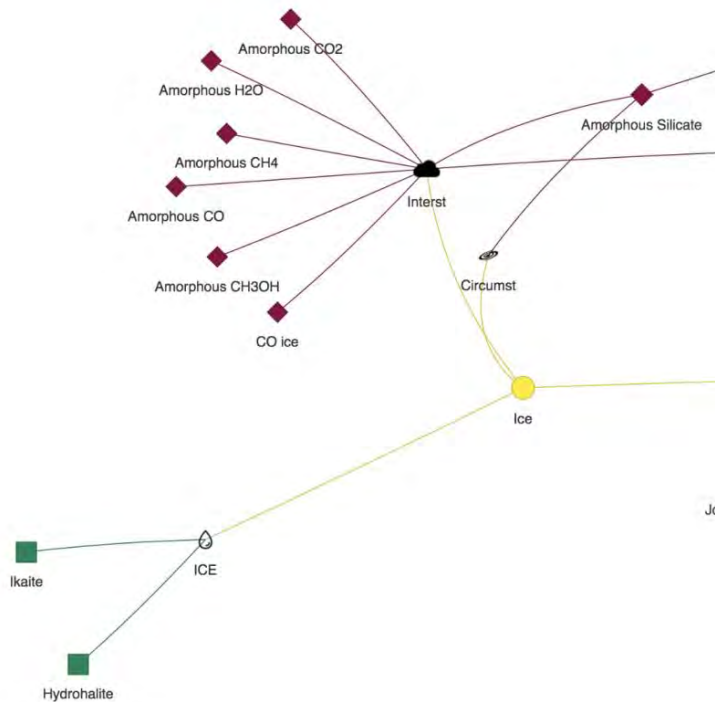
821

A.



822

B.

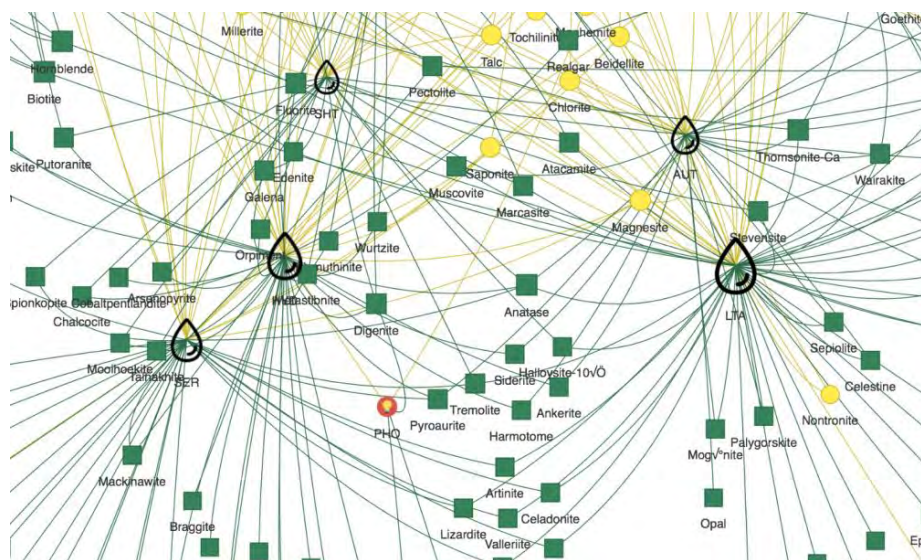


823

C.

824

D.



825 Figure 2. Selected areas of the bipartite network graph (Figure 1).

826 **A.** Impact minerals from meteorites (planet-shaped icon on the right) and terrestrial sites
827 (planet-shaped icon on the left) largely overlap. Five terrestrial impact minerals are predicted to
828 have occurred on early Hadean Earth but have not yet been found in meteorites, whereas four
829 meteorite impact minerals related to shocked iron meteorites are not yet known from terrestrial
830 settings. Only five minerals, including diamond, clinoenstatite, and cordierite, connect these
831 impact phases with the rest of the graph.

832 **B.** Primary igneous phases from early Earth, represented by volcano-shaped icons (UMA =
833 ultramafic rocks; MAF = mafic rocks; SIL = quartz normative rocks; ANO = anorthosite),
834 include many phases that are also found in the mafic lithologies of achondrite meteorites, and
835 therefore form a centralized cluster of green and yellow nodes.

836 **C.** Low-temperature and low-pressure condensates (“ices”) form a distinct cluster of phases in
837 the lower left of the network graph. Water ice provides important connections among interstellar
838 (cloud icon), circumstellar (disk icon), cold asteroidal surface (planet icon), and terrestrial ice
839 (droplet icon) environments.

840 **D.** Numerous minerals formed by water-rock interactions on Earth form a distinct cluster of
841 green nodes near the bottom of the graph. The five droplet-shaped icons are separated into two
842 lower-temperature formation processes on the right (AUT = authigenic; LTA = low-temperature
843 alteration) and three higher-temperature processes on the left (SER = serpentinite; HYD =

844 hydrothermal vein; SHT = seafloor hydrothermal vent). Relatively few of these phases are also
845 known from meteorites.

846

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

853 Another group of minerals forms a distinct cluster of phases formed by water-rock
854 interactions (Figure 2D). These minerals, represented by green nodes near the bottom of the
855 graph, are linked to five droplet icons. These icons are further clustered into two lower-
856 temperature formation processes on the right-hand side of Figure 2D (representing authigenic
857 mineralization and low-temperature alteration) and three higher-temperature processes on the
858 left-hand side (including serpentinization, hydrothermal vein deposition, and seafloor
859 hydrothermal vents). Note that relatively few of these phases are also known from meteorites, so
860 they appear as green nodes that tend to be significantly separated from the more centralized
861 phases that share meteorite and Earth origins (i.e., yellow nodes).

862

863 *Minerals and the origins of life:* The paleomineralogy of the Hadean Eon has attracted
864 significant attention in the context of life's origins, because most biogenesis models posit an
865 origin event prior to 4.0 Ga. A wide variety of minerals have been invoked in origins scenarios,
866 some of them not included in lists of early Hadean species (Hazen 2013). For example, phases
867 with postulated catalytic sites such as borates, molybdates, and phosphates (Ricardo et al. 2004;

868 Kim et al. 2016; Ziegler et al. 2018) are not in our inventories. Even if our Hadean mineral
869 catalog is too limited, and minerals such as borates or molybdates were in fact present prior to
870 4.37 Ga, they would have been extremely minor phases with trivial total volumes. Is this lack an
871 impediment to essential origins-of-life chemical processes?

872 We now realize that any chemical element that may have played a critical role in biology
873 today was abundantly available for prebiotic chemistry in the earliest Hadean Eon, if not as an
874 essential element in a Hadean mineral, then as a trace or minor element in one or more common
875 rock-forming minerals (Morrison et al. 2018; Hazen and Morrison 2021b). For example, boron
876 with an average crustal abundance of 10 parts per million (ppm) is typically present at > 100
877 ppm in augite. Likewise, phosphorus occurs in concentrations > 1000 ppm in olivine,
878 plagioclase, and basaltic glass. Indeed, a range of biologically essential transition elements,
879 including Co, Ni, Cu, Zn, and Mo, were ubiquitous as trace elements in rock-forming oxides and
880 silicates at concentrations many times their average crustal abundance (Hazen and Morrison
881 2021b; their Table 2.1). In each of these (and many more) instances, common rock-forming
882 minerals are orders-of-magnitude larger crustal reservoirs of rare elements than any other
883 mineralogical source. We conclude that common Hadean minerals provided a diverse and
884 omnipresent range of potentially catalytic surface sites for biogenesis – a facet of prebiotic
885 chemistry that has yet to be explored.

886

887

ACKNOWLEDGMENTS

888 We are especially grateful to Richard Carlson for valuable discussions and a detailed review
889 of an early version of this contribution. Alexander Evans, Edward Grew, Timothy Grove, Jihua
890 Hao, Peter Kelemen, Craig Manning, Karyn Rogers, Dimitri Sverjensky, Lindy Elkins-Tanton,
891 and Michael Walter provided expert advice on aspects of early Earth petrology and
892 geochemistry. We also thank Associate Editor Steven Simon, and reviewers Kent Condie and
893 George Harlow for their thorough, thoughtful, and constructive reviews.

894

895

FUNDING

896 Studies of mineral evolution and mineral ecology have been supported by the Alfred P. Sloan
897 Foundation, the W. M. Keck Foundation, the John Templeton Foundation, the NASA
898 Astrobiology Institute ENIGMA team, a private foundation, and the Carnegie Institution for
899 Science. Any opinions, findings, or recommendations expressed herein are those of the authors
900 and do not necessarily reflect the views of the National Aeronautics and Space Administration.

901

902

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

Formational Environment	#Species*	#Cumulative**	Refs***
<i>Primary igneous minerals</i>	<u>83</u>		
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
<i>Hydrothermal minerals</i>	<u>98</u>		
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
<i>Thermal or aqueous alteration of prior minerals</i>	<u>106</u>		
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
<i>Surficial mineral-forming processes</i>	<u>109</u>		
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

* Detailed lists of minerals and their paragenetic modes appear in Supplementary Table 1.

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

*** 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://rruff.info/ima> and <https://mindat.org>, and references therein (accessed 7 August 2021).

Numbered 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 = Haymond and Kastner (1981); 16 = Palandri and Reed (2004); 17 = Lowell and Rona (2002); 18 = Holm et al. (2015); 19 = Bowles et al. (2011); 20 = Aquioano et al. (2021);

1641 21 = Tschauner (2019); 22 = Essene and Fisher (1986); 23 = Hess et al. (2021); 24 = Holser
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