1 REVISION #1A—June 26, 2021—Submitted to American Mineralogist 2 On the paragenetic modes of minerals: 3 A mineral evolution perspective 4 5 ROBERT M. HAZEN 1,* AND SHAUNNA M. MORRISON 1 6 ¹Earth and Planets Laboratory, Carnegie Institution for Science, 7 8 5251 Broad Branch Road NW, Washington DC 20015, U. S. A. 9 10 **ABSTRACT** 11 A systematic survey of 57 different paragenetic modes distributed among 5659 mineral 12 species reveals patterns in the diversity and distribution of minerals related to their 13 evolving formational environments. The earliest minerals in stellar, nebular, asteroid, and 14 primitive Earth contexts were dominated by relatively abundant chemical elements, 15 notably H, C, O, Mg, Al, Si, S, Ca, Ti, Cr, and Fe. Significant mineral diversification 16 subsequently occurred via two main processes, first through gradual selection and 17 concentration of rarer elements by fluid-rock interactions (for example, in hydrothermal 18 metal deposits, complex granite pegmatites, and agaitic rocks), and then through near-19 surface biologically-mediated oxidation and weathering. 20 We find that 3349 mineral species (59.2 %) are known from only one paragenetic 21 context, whereas another 1372 species (24.2 %) are associated with two paragenetic 22 modes. Among the most genetically varied minerals are pyrite, albite, hornblende, 23 corundum, magnetite, calcite, hematite, rutile, and baryte, each with 15 or more known 24 modes of formation. 25 Among the most common paragenetic modes of minerals are near-surface weathering/oxidation (1998 species), subsurface hydrothermal deposition (859 species), and condensation at volcanic fumaroles (459 species). In addition, many species are associated with compositionally extreme environments of highly differentiated igneous lithologies, including agaitic rocks (726 species), complex granite pegmatites (564 species), and carbonatites and related carbonate-bearing magmas (291 species). Biological processes lead to at least 2707 mineral species, primarily as a consequence of oxidative weathering but also through coal-related and other taphonomic minerals (597 species), as well as anthropogenic minerals, for example as byproducts of mining (603 minerals). However, contrary to previous estimates, we find that only ~34% of mineral species form exclusively as a consequence of biological processes. By far the most significant factor in enhancing Earth's mineral diversity has been its dynamic hydrological cycle. At least 4583 minerals – 81 % of all species – arise through waterrock interactions. A timeline for mineral-forming events suggests that much of Earth's mineral diversity was established within the first 250 million years. If life is rare in the universe, then this view of a mineralogically diverse early Earth provides many more plausible reactive pathways over a longer timespan than previous models. If, however, life is a cosmic imperative that emerges on any mineral- and water-rich world, then these findings support the hypothesis that life on Earth developed rapidly in the early stages of planetary evolution.

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48 **Keywords:** philosophy of mineralogy; classification; mineral evolution; natural kinds;

meteorite mineralogy; thermal metamorphism; aqueous alteration; biomineralization

^{*}E-mail: rhazen@carnegiescience.edu. ORCID 0000-0003-4163-8644

50 Introduction

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The minerals that form Earth arose from a variety of physical, chemical, and biological processes over a time span now known to exceed 7 billion years (Hazen et al. 2008; Heck et al. 2020). Identifying and systematizing these mineral-forming processes is 54 key to understanding planetary evolution through deep time. Accordingly, we have 55 conducted a comprehensive survey of the modes of formation (i.e., "paragenetic modes" 56 - see below) of 5659 mineral species approved by the International Mineralogical 57 Association's Commission on New Minerals, Nomenclature and Classification (IMA-58 CNMNC). The underlying motivation for this effort is to understand how the diversity 59 and distribution of minerals have changed through deep time and to propose a system of mineral classification complementary to IMA-CNMNC protocols that reflects mineral origins in the context of evolving terrestrial worlds. 62 Hazen, Morrison, and colleagues have introduced an "evolutionary system of mineralogy," which classifies "historical natural kinds" (Boyd 1991, 1999; Hawley and Bird 2011; Magnus 2012; Khalidi 2013; Ereshevsky 2014; Godman 2019; Cleland et al. 2021) based on modes of mineral formation, as manifested in their distinctive combinations of physical and chemical attributes (Hazen 2019; Hazen and Morrison 67 2020, 2021; Morrison and Hazen 2020, 2021; Hazen et al. 2021). In this effort, we adopt the principle that any alternative system of mineral classification should complement and amplify IMA-CNMNC protocols (Hatert et al. 2021; Hazen 2021), as they are based on 70 the rigorous time- and origin-independent attributes of idealized chemical compositions and crystal structures (e.g., Burke 2006; Mills et al. 2009; Schertl et al. 2018; Cleland et 72 al. 2021).

The alternative evolutionary approach to mineral classification relies on identifying diagnostic suites of mineral properties and the inferred historical processes by which those distinctive properties arose. Accordingly, it is important to enumerate the variety of mineral paragenetic modes, as well as the temporal context of those diverse mechanisms of formation. The principal objective of this contribution is to identify and catalog the paragenetic modes of all known minerals and to attempt to place those mineral-forming mechanisms in the chronological context of Earth's 4.567-billion-year evolution.

What is a paragenetic mode?

The term "paragenesis" has been applied in different ways to minerals and their formation. Paragenesis is often used in the context of a specific mineral assemblage: "A characteristic association or occurrence of minerals or a mineral assemblage, especially in ore deposits, connoting a specific equilibrium assemblage or contemporaneous formation" (https://mindat.org, accessed 26 June 2021). "Paragenesis" or "paragenetic sequence" is also commonly used to mean the sequence of mineral formation in a suite of rocks, such as a regional metamorphic terrain with a range of temperature-pressure conditions or an ore deposit with stages of mineralization (e.g., Craig and Vaughan 1994; Guilbert and Park 2007). And, in a broader context, paragenesis "may be applied to any sequence or assemblage of minerals related by common formation conditions" (Ebel and Kamilli 2018).

Our definition of "paragenetic mode" is most closely related to the latter sense of the term. We define a "mineral paragenetic mode" as a natural process by which a collection of atoms in solid and/or fluid form are reconfigured into one or more new solid forms.

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This definition emphasizes an individual mineral's mode of formation rather than a mineral assemblage or a sequence of mineralization. Consequently, paragenetic modes encompass a wide variety of mineral formation processes, including the formation of primary phases by condensation from a gas; the crystallization of minerals through evaporation of an aqueous solution; the transformation of preexisting phases by lightning, impacts, or other sudden events; and biomineralization. In its broadest sense, our definition of paragenetic mode applies to processes that form a range of solids that are not usually incorporated in IMA-CNMNC protocols, including volcanic glass, kerogen, amber, and other amorphous and/or biologically-formed phases. Note that sharp boundaries do not always exist between natural crystalline compounds and other solid phases; for example, we are still grappling with how to incorporate biological crystal/organic composite materials of the Phanerozoic Eon, such as bones, teeth, and shells. Our definition of paragenetic modes implicitly requires knowledge of three aspects of the mineral-forming process. (1) The initial state of the system: Minerals form from precursor chemical systems at a wide range of initial pressure-temperature-composition (P-T-X) conditions. It is often useful to define minerals that emerge through condensation or precipitation from a gas, liquid, or supercritical fluid as "primary minerals," whereas phases that arise through modification of preexisting minerals (the majority of species) are called "secondary minerals." Note, however, that intermediate formation processes may occur and the distinction between primary and secondary is not always unambiguous (e.g., Hazen and Morrison 2021).

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(2) The mechanism of transformation: Mineral-forming mechanisms range from rapid energetic events, such as bolide impacts and lightning strikes with durations on the order of seconds or less, to much more gradual processes, such as solid-state reactions that occur during regional metamorphism or fluid-rock interactions associated with metasomatism. These mechanisms also operate at diverse spatial scales from micrometers (e.g., microbial biomineralization) to hundreds of kilometers (regional metamorphism). (3) The resulting solid phases: Each combination of initial state and transformation mechanism yields one or more mineral phases. These three characteristics of the paragenesis of every mineral – initial state, transformation mechanism, and final state – are reflected in typical descriptions of mineral occurrences, notably in the *Handbook of Mineralogy* (Anthony et al. 1990-2003) and Rock-Forming Minerals (Deer et al. 1982-2013). For example, periclase (MgO) is "a relatively high temperature mineral, resulting from the metamorphism of dolomites and magnesian limestones" (Bowles et al. 2011), whereas malachite [Cu₂(CO₃)(OH)₂] is "a common secondary mineral formed in the oxidation zone of copper deposits" (Anthony et al 2003). Uncertainties related to the classification and timing of paragenetic modes In attempting to classify the paragenetic modes of minerals, we have adopted four general principles:

1. Every mineral species approved by the IMA-CNMNC must be associated with at 140 141 least one paragenetic mode (e.g., the copper arsenate mineral popovite forms by 142 sublimation at volcanic fumaroles). 143 2. Each paragenetic mode applies to a group of minerals that share a formation 144 process (e.g., more than 400 minerals form by sublimation at volcanic fumaroles). 145 3. Mineral-forming environments that represent continuous variations of temperature 146 and pressure, for example regional metamorphic facies (greenschist and 147 amphibolite) or hydrothermal zones (epithermal and mesothermal) have been 148 lumped together. 149 4. Related mineral-forming environments that represent an evolutionary sequence 150 have been split; for example, ultramafic igneous rocks are distinguished from 151 mafic igneous rocks that often arise by decompression melting of ultramafic rocks. 152 In spite of these guidelines, our preliminary chronological tabulations of the 153 paragenetic modes of minerals (Table 1; Supplementary Database 1) are subjective in at 154 least two important respects related to: (1) the classification of paragenetic modes, and (2) the relative timing of the initiation of Earth's principal mineral-forming processes. 155 156 Consequently, enumerating and defining different paragenetic modes must be an ongoing 157 process that involves a broad spectrum of mineralogists and petrologists. In this context, 158 we welcome advice and discussions regarding our provisional classification of 159 paragenetic modes. 160 <u>The classification of paragenetic modes:</u> A significant source of subjectivity in our study 161 162 is intrinsic to any classification system – to what extent does one lump or split the varied 163 paragenetic modes of minerals? At the broadest scale, descriptors such as "intrusive

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igneous," "regional metamorphic," and "hydrothermal alteration" are commonly associated with the formation of minerals in different environments. These and similar general terms may be applied to the characterization of paragenetic modes of most minerals (e.g., Philpotts and Ague 2009; Wenk and Bulakh 2016). However, any attempt to further subdivide mineral formation mechanisms, for example into compositional categories of intrusive igneous rocks, facies of regional metamorphism, or gradations of aqueous mineral alteration among metasomatic, hydrothermal, authigenic, and nearsurface weathering processes, will be inherently subjective because minerals form over continuous *P-T-X* regimes. Three prior efforts that detail systems of paragenetic modes for important subsets of minerals exemplify the utility and diversity of specialized approaches that can be developed. Guilbert and Park (2007) presented a "litho-tectonic" classification that recognizes more than 100 paragenetic categories of ore deposits based on a hierarchy of (1) tectonic setting (e.g., mid-ocean ridge; cratonic; convergent margin), (2) host lithologies (granite; massive sulfide; skarn), and (3) commodities (copper-gold; coal; chromite). In their system, Guilbert and Park differentiate hydrothermal "Cyprus-type" sulfide deposits from those at mid-ocean ridges, "proximal" massive sulfide deposits from those at subducting margins, and sulfide deposits at back-arc basins versus those from cratons. This detailed and comprehensive system is undoubtedly useful for placing ore deposits in their plate tectonics contexts. However, it is not as appropriate for applications to the full sweep of Earth's evolution for at least three reasons. First, Guilbert and Park subdivide some types of mineralization, including volcanogenic massive sulfide deposits, iron formations, and carbonatites, into multiple tectonic

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contexts (e.g., cratons, back-arc basins, or subducting margins) – divisions that only apply to Earth after the initiation of plate tectonics. By contrast, we differentiate paragenetic modes primarily based on pressure-temperature-composition regimes, as opposed to tectonic settings. Second, they narrowly subdivide many deposit types into compositional groups (e.g., Cu, Cu-Mo, Mo, and Cu-Au porphyry copper deposits are listed separately), whereas we do not employ composition as extensively to distinguish among deposit types. And third, numerous non-commercial paragenetic modes, including pre-terrestrial nebular minerals, products of near-surface weathering, metamorphism, and biomineralization, are understandably not included in the Guilbert and Park (2007) economic classification. Another specialized list of paragenetic modes was offered in the comprehensive survey of meteorite minerals by Rubin and Ma (2021, their chapter 10). They catalog 22 paragenetic modes representing minerals from the full range of meteorite finds and falls, including eight processes related to primary crystallization from gases or melts of different compositions, six variants of aqueous and/or thermal secondary alteration, four variants of solid-state exsolution, shock metamorphism, annealing of amorphous materials, and two forms of meteorite weathering (space weathering versus terrestrial alteration). This revealing list is illuminating in terms of the variety of processes that might produce new solid phases; however, in many instances the exact process by which a meteorite mineral formed is ambiguous and a matter of debate, at times because multiple mechanisms may come into play simultaneously or sequentially. We consolidate Rubin and Ma's 22 modes into seven subsets that we apply specifically to meteorite minerals: condensation of refractory phases in stellar atmospheres; condensation of

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molecular solids in interstellar environments; condensation from nebular gas; crystallization from chondrule melts; primary minerals formed during asteroid differentiation; thermal, aqueous, and impact alteration of prior meteorite phases in an asteroid body; and terrestrial weathering. A third specialized tabulation of mineral-forming processes was provided by Hill and Forti (1997), who illustrate more than 20 paragenetic modes associated with cave minerals. Their comprehensive survey of 255 cave mineral species distinguishes formation by varied mineral-precipitating aqueous fluids (e.g., rich in silica, carbonate, sulfate, and/or metals); sublimates from subsurface volcanic fumarole vents; oxidation or reduction of prior minerals; bacterial fixation, for example of Fe or Mn minerals; subsurface evaporation to form halides or carbonates; numerous phosphate, nitrate, and organic minerals related to reactions with guano; and freezing of ice. They also present a division into six types of aqueous depositional environments: flowing water, dripping water, pool water, seeping water, condensation water, and thermal water. Like Hill and Forti (1997), we do not consider "cave minerals" a separate paragenetic mode; rather we lump subsets of these shallow subsurface minerals with minerals formed by analogous subaerial processes. Thus, we include halite formed by evaporation in a dry cave with other evaporite minerals. Similarly, we lump subsurface cave fumarole minerals with those that occur at volcanic vents at the surface. Our preliminary tabulation recognizes 57 paragenetic modes, each assigned a reference number (cited as "[#xx]" in this contribution; see Table 1). This classification of paragenetic modes is admittedly subjective in several respects. In particular, when minerals form over a wide range of pressures, temperatures, compositions, and/or time

we have, of necessity, selected somewhat arbitrary subdivisions based on the following criteria:

- 1) Depth of formation: In most instances, we distinguish near-surface mineralization that is presumed to form in direct atmospheric contact, either at the surface or in shallow subsurface settings (e.g., volcanic lavas [#9], fumaroles [#11], hot-spring precipitates [#14], subaerial aqueous alteration [#16], and evaporites [#25]), versus subsurface processes not in atmospheric contact (e.g., intrusive igneous formations [#19], subsurface aqueous alteration [#22], primary hydrothermal vein minerals [#33], and regional metamorphism [#40]). Exceptions include Earth's earliest lithologies (most of which are still being produced today) ultramafic and mafic igneous rocks for which we lump intrusive and extrusive lithologies (e.g., peridotite and komatiite [#7], and basalt and gabbro [#8]).
- 2) Metamorphic facies: Rather than differentiating among all facies of regional metamorphic rocks, we recognize three broad *P-T* trends [e.g., as illustrated by Philpotts and Ague (2009), their figure 16.6]. We lump facies of regional metamorphic rocks (e.g., greenschist, amphibolite, and granulite facies) into one paragenetic mode [#40]. We distinguish those facies from metamorphic rocks formed at relatively high pressure and low temperature, including blueschist, eclogite, and ultrahigh-pressure (UHP) facies [#39]; these lithologies are tied to subduction tectonics and thus may be constrained to post-Archean time intervals of Earth history. Finally, in the case of very low-pressure, high-temperature "pyrometamorphic" minerals (Grapes 2006), we recognize four distinct paragenetic environments, including: (1) thermally metamorphosed xenolith minerals (sanidinite,

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or sometimes hornfels, facies) in volcanic and hypabyssal rocks [#9]; (2) near-surface minerals altered by regional fires, as exemplified by the distinctive mineralogy of the Hatrurim Formation in the Middle East (Gross 1977; Sokol et al. 2019) [#51]; (3) anthropogenic pyrometamorphic minerals formed by coal mine fires [#54]; and (4) slag minerals associated with the smelting of ores [#56]. In the cases of regional and high-pressure metamorphic rocks, our conservative approach could be expanded by further subdivision into multiple facies in a future treatment.

3) Igneous lithologies: The classification of igneous rocks is a classic problem with no unique solution. At one extreme, Johannsen (1932–1938) proposed hundreds of rock types based on modest variations in mineralogy, bulk composition, and textures. Significant order to the problem was achieved by the Subcommission on the Systematics of Igneous Rocks of the International Union of Geological Sciences (the "IUGS classification": Streckeisen 1976, 1979; Le Bas et al. 1986; Le Bas and Streickeisen 1991), which recognizes approximately 60 igneous rock types, again based on mineralogy, composition, and texture. We adopt a more parsimonious approach, with eight paragenetic modes chosen to reflect diagnostic suites of igneous minerals. Ultramafic igneous rocks such as peridotite, pyroxenite, and komatiite [#7], which are composed primarily of Mg-Fe minerals, represent the earliest nearsurface rocks on Earth, though these lithologies still form today. We distinguish ultramafic lithologies from plagioclase-rich mafic igneous rocks such as basalt and gabbro, which are derived primarily from decompression melting of prior ultramafic lithologies [#8]. We list both intrusive granitic igneous rocks [#19] and their acidic volcanic equivalents such as rhyolite and dacite [#20], and we differentiate mineral-

rich complex pegmatites of granitic [#34] and agpaitic [#35] rocks. We also recognize mineralogically-distinctive carbonatites and related carbonate-rich igneous rocks [#36], as well as layered igneous formations because of their unusual richness in minerals of platinum group elements (PGE; O'Driscoll and VanTongeren 2017) [#37]. Five additional paragenetic modes are closely related to igneous processes: pyrometamorphosed xenoliths in lava [#9], basalt-hosted zeolite minerals [#10], volcanic fumarole minerals [#11] and [#45], and the highly-altered ultramafic rocks of obducted ophiolites [#38]. Note that we do not treat a number of important igneous lithologies, including andesite, anorthosite, monzonite, and syenite (Streckeisen 1976; Le Bas and Streckeisen 1991; Ashwal 1993; Philpotts and Ague 2009), as separate paragenetic modes because they do not appear to incorporate new mineral species or distinct formation mechanisms.

- 4) Water-rock interactions: Mineral formation processes related to water-rock interactions pose a significant challenge in classifying mineral paragenetic modes. A number of potentially ambiguous and partially overlapping terms, including aqueous alteration, authigenesis, diagenesis, hydrothermal mineralization, metasomatism, and serpentinization, have been applied to these formation environments of minerals (Heinrich and Henley 1989; Pirajno 2009; Steele-MacInnis and Manning 2020). We are not able to fully resolve this difficulty, but we have adopted the following definitions:
 - <u>Authigenesis</u>: Authigenesis refers to mineral formation *in situ* by direct precipitation from an aqueous solution, for example as a carbonate cement in detrital sediments. We apply this term exclusively to low-T (< ~100 °C)

sedimentary environments, in contrast to some prior uses in metamorphic petrology. We distinguish marine authigenesis [#17], which must have commenced early in the Hadean Eon, from authigenesis in terrestrial sediments [#24].

- <u>Diagenesis</u>: Diagenesis refers to the alteration of sediments in an aqueous environment by increasing *T* and *P*, resulting in compaction, lithification, dissolution/precipitation reactions, and some alteration of mineral chemistry by interactions with fluids. Our tabulations do not include diagenesis as a separate paragenetic process, as it may be viewed as the initial stages of metamorphism prior to the formation of new mineral assemblages.
- Hydrothermal mineralization: We define hydrothermal mineralization as any precipitation of minerals from an aqueous phase that is > 100 °C or, in the case of near-surface waters, significantly above ambient temperature. We distinguish among mineralization associated with near-surface hot and/or subaerial boiling fluids such as hot springs and geysers [#14]; seafloor hydrothermal vents, known as black smokers and white smokers [#15]; and subsurface mineralization, usually deposited in veins and other fracture systems [#12] and [#33]. Hydrothermal minerals are typically compositionally distinct from their host lithologies. Note that we do not differentiate among different *P-T* regimes of subsurface hydrothermal mineralization (e.g., epithermal, mesothermal, and hypothermal).
- Metasomatism: Metasomatism is a general term for the subsurface hydrothermal alteration of minerals through mass transfer in an open system

(Harlov and Austrheim 2013). As such, the term can be applied to varied chemical processes (e.g., hydration/dehydration, dissolution/precipitation, and ion exchange reactions). Metasomatism may affect the full spectrum of subsurface lithologic settings, including metamorphism and diagenesis of sediments, alteration of plutonic and volcanic rocks, skarn formation, and alteration of a wide variety of ore deposits. Given this broad umbrella of processes and environments, "metasomatism" is not particularly helpful as a paragenetic descriptor. Therefore, we employ it in only in the specific case of "mantle metasomatism" (Luth 2003; O'Reilly and Griffin 2012), which is a term well embedded in the literature related to the alteration of mantle lithologies by complex C-O-H fluids [#41].

- Serpentinization: Serpentinization is the low-*T* (typically < 100 °C, but at times to T > 200 °C) aqueous alteration process by which anhydrous ferromagnesian minerals in mafic and ultramafic rocks are transformed to hydrous phases, including serpentine polytypes and brucite (Shrenk et al. 2013). Serpentinization is just one of many mineral-producing water-rock interactions; however, it is possibly the most ubiquitous chemical reaction on wet terrestrial planets (e.g., Holm et al. 2015), and it has transformed at least 70 % of Earth's crust throughout its 4.5-billion-year history [#13].
- Aqueous alteration: "Aqueous alteration" is the most general term for any process that changes minerals by interactions with a water-based solution, irrespective of *P-T-X* conditions. We adopt "aqueous alteration" as a fallback term for the paragenesis of hundreds of mineral species that do not clearly fit

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one of the above categories of water-rock interaction, especially when reported details of formation processes are vague. We recognize five subsets of low-T (< 100 °C) aqueous alteration, based on age and depth of formation: subsurface and subaerial aqueous alteration of Hadean lithologies (> 4 Ga) [#16]; subsurface aqueous alteration, prior to the Great Oxidation Event (GOE, >2.5 Ga) [#22]; subaerial aqueous alteration, pre-GOE [#23]; subsurface aqueous alteration, post-GOE (< 2.5 Ga) [#46]; and subaerial aqueous alteration, post-GOE [#47]. In addition to the above paragenetic mechanisms, we recognize five near-surface processes related to water-rock interactions that produce distinctive suites of minerals: freezing of aqueous solutions [#18]; pre-biotic surface precipitation of carbonate, phosphate, and iron formations [#21]; evaporite minerals [#25]; seafloor manganese nodules [#42]; and leaching zone soil minerals, including laterites and bauxites [#48]. 5) Composition: The lumping and splitting of compositional variants is an admittedly subjective aspect of our proposed system. For example, we distinguish between minerals formed in complex granite pegmatites [#34] versus against pegmatites [#35], because the compositions of their host lithologies (and the resulting mineral species) are dramatically different, even though the mechanisms of mineral formation are similar. We divide contact metamorphic deposits into two somewhat overlapping compositional groups: 356 metamorphosed carbonate (i.e., skarn), phosphate, and iron-formation minerals [#31], are treated as distinct from 412 phases associated with mineral-rich metamorphic Ba, Mn, Pb, and/or Zn deposits [#32]. Also, as noted above, we separate 129 hydrothermal sulfides with common transition

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metals [#12] from most other chalcogenides [#33] on the basis of their assumed chronology. However, with the exception of distinct platinum groups element (PGE) enrichments in layered intrusions [#37], we do not further subdivide hydrothermal metal deposits according to their principal metals or lithologic context.

6) Chronology – crust formation: In several instances, we have split minerals derived from mafic/ultramafic lithologies, and thus assumed to have first appeared early in the Hadean Eon (Stage 3 of Table 1), from minerals likely derived from subsequent granitic lithologies and the formation of continental crust (Stage 4) and/or after the GOE (Stage 7). Thus, we distinguish minerals formed by authigenesis in marine sediments as early as the Hadean Eon [#17] from authigenic minerals of Earth's earliest continental crust, which likely appeared later [#24]. Similarly, we differentiate the presumed earliest suites of Hadean minerals formed by subaerial aqueous alteration of basaltic crust [#16] from those that more likely first formed subsequently in granitic crust [#23] or after the GOE (see below) [#47]. We also split (with significant uncertainties) some presumably ancient hydrothermal vein sulfides [#12] versus other chalcogenides [#33], because the extensive development of sulfide deposits appears to predate that of other much less abundant chalcogenides, such as those dominant in As, Sb, Se, and Te. Note that in all of these examples, minerals that first formed early in the Hadean Eon continue to form today; our sequence of mineral paragenetic modes thus reflects a gradual accumulation of more and more mineral-forming processes, rather than a sequential replacement of processes.

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7) Chronology – the Great Oxidation Event: Late Archean (< 3 Ga) atmospheric oxygenation (the "Great Oxidation Event" or GOE) represents a major transition in the formation of near-surface minerals on Earth. Therefore, in four instances we distinguish suites of relatively reduced, near-surface/subaerial phases, presumably formed prior to the GOE from suites of more oxidized minerals that most likely formed after the GOE. We split fumarolic minerals into more reduced phases [#11], such as sulfides that were likely associated with volcanism early in the Hadean Eon, and more oxidized species such as sulfates and arsenates [#45], that presumably formed after atmospheric oxygenation. We differentiate between low-temperature, subsurface aqueous alteration prior to the GOE [#22] and post-GOE [#46]. Similarly, we divide low-temperature, subaerial aqueous alteration pre-GOE [#23] and post-GOE phases [#47]. We also enumerate 11 minerals formed by anaerobic microbial metabolism prior to the GOE [#44], compared to 77 biominerals produced directly through cellular processes post-GOE [#49]. 8) Near-surface oxidation/weathering: Because of the large number (~ 2000 species) of secondary minerals formed by near-surface oxidation, weathering, and hydration [#47], we have divided these diverse phases into nine subgroups designated [#47a] to [#47i] based on mineral chemistry (thus they are not additional paragenetic modes).

Most post-GOE weathered phases fall into two or more of these compositional subgroups. For example, the rare mineral bluelizardite [Na₇(U⁶⁺O₂)(SO₄)₄Cl'2H₂O] is included in four compositional subcategories: near-surface hydration [#47a],

sulfates [#47b], uranyl (U⁶⁺) minerals [#47f], and halogen-bearing phases [#47g].

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The relative timing of Earth's principal mineral-forming processes: An important objective of our study is to present a chronological tabulation of modes of mineral formation, with quantitative geochronological constraints where possible. However, this effort is faced with significant uncertainties. In a few instances, for example with primary meteorite minerals [#1] to [#5] (> 4.56 Ga); Phanerozoic biomineralization and taphonomic minerals (i.e., minerals formed via decay/alteration of biological materials) [#49], [#52], and [#53] (< 541 Ma); coal minerals [#50] (< 360 Ma); and anthropogenic minerals [#54] to [#57] (< 10 Ka), the ages of minerals are well defined by the nature of the processes in question. In addition, over the past decade we have developed the Mineral Evolution Database (MED; https://rruff.info/evolution, accessed 17 March 2021; Golden et al. 2016; Golden 2020), with more than 190,000 minerals species/age/locality data for more than 1000 different mineral species. However, in the cases of most mineral species and their formation mechanisms, the absolute and relative timings of paragenetic modes are poorly constrained. Two well-known factors contribute to these uncertainties. First is the paucity of any geological formations older than ~3.5 Ga; therefore, solid evidence for the formation and timing of Hadean and Paleoarchean minerals is literally all but lacking. The ages of many mineral-forming processes might be inferred if we knew the timings of significant episodes in Earth history, such as the formation of continents, the establishment of oceans, and the transition from vertical plume tectonics to lateral plate tectonics. However, the nature and timing of these and other events from Earth's first billion years are matters of intense ongoing debates. Among the uncertainties are:

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The composition and extent of Earth's earliest crust: The mineral evolution of differentiated Earth began with subaerial solidification of the magma ocean that formed immediately after the Moon-forming impact (> 4.50 Ga; Barboni et al. 2017; Thiemans et al. 2019), coupled with initiation of mantle convection, possibly under a "stagnant lid" (i.e., prior to significant recycling of surface layers; e.g., Debaille et al. 2013; Piper 2013; Stern 2018; Korenaga 2021). General agreement exists that Earth's earliest crust featured globe-spanning mafic/ultramafic igneous lithologies; however, significant debate remains regarding that crust's composition and thickness - parameters that may have strongly influenced the earliest stages of mineral evolution (Rollinson 2007b; Korenaga 2021). The earliest crust was likely more mafic (i.e., with a higher average Mg content) than today (Taylor and McLennan 1995; Kemp and Hawksworth 2003; Keller and Schoene 2012). If a relatively thick mafic crust (i.e., similar in composition to modern oceanic crust) prevailed, then a gradual tectonic transition from stagnant lid to subduction seems plausible. If, on the other hand, Earth's first crust was dominated by a relatively thin ultramafic layer, as advocated by Korenaga (2021), then sinking dense crustal slabs may have triggered an active early style of subduction-driven plate tectonics in the Hadean Eon. In this study, we assume that some combination of mafic and ultramafic crustal lithologies dominated Earth's earliest mineral diversity by ~4.50 Ga, without adopting a position on the compositional and tectonic details. The composition and extent of Earth's earliest oceans: Most models of early Earth posit the rapid evolution of a hydrosphere, culminating in globe-spanning oceans by 4.45 Ga (Wilde et al. 2001; Mojzsis et al. 2001; Elkins-Tanton 2011). Anoxic

Hadean oceans must have differed significantly from more recent marine environments. For example, estimates of Hadean ocean chemistry suggest significantly higher salinity than the modern oceans (Holland 1984; Knauth 2005; Marty et al. 2018) – conditions that might have led to enhanced evaporite deposition at coastal margins. In this study, we assume that oceans were well established by 4.45 Ga.

The timing and extent of continental crust formation: A major uncertainty is the

timing of initiation and evolution of buoyant, felsic continental crust that was relatively enriched in incompatible elements — a significant source of mineral diversity. Stable, long-lived continental crust is thought to form principally through extensive partial melting of a hydrated mafic layer in the upper mantle. Virtually all models posit formation of some felsic crust by 4.4 Ga, but estimates of the rate of subsequent continental "net crustal growth" vary wildly. At one extreme, some authors suggest rapid granitic production, achieving close to modern extent of continental crust by the early Hadean Eon (Armstrong 1991; Rosas and Korenaga 2018; Guo and Korenaga 2020). Others argue for a more gradual development of net crustal volume, with modern levels not achieved until the mid-Proterozoic or later (Belousova et al. 2010; Dhuime et al. 2012; Greber et al. 2017; see Korenaga 2018, his Figure 1 and references therein). In this study, we assume that felsic continental crust sufficient to enhance Earth's mineral diversity developed by 4.40 Ga, without weighing in on the debate regarding the rate of continental evolution.

• The extent of dry land: Significant uncertainties exist regarding the volume and depth of Hadean surface waters. Notably, recent models suggest that the Hadean

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ocean may have held significantly more water, perhaps twice today's volume (Kurokawa et al. 2018; Dong et al. 2021), as a consequence of the relatively hot, and therefore dry, peridotitic mantle prior to 4 Ga. Subsequent mantle hydration through plate tectonics gradually decreased the ocean's volume to modern levels (Jarrad 2003; Korenaga 2008; Korenaga et al. 2017; Rosas and Korenaga 2021). A voluminous early ocean, possibly coupled with less extreme topography owing to a steeper geothermal gradient and/or lack of orogenesis (e.g., Tang et al. 2021), may have resulted in a largely submerged Hadean world with extensive serpentinization and other water-rock interactions (Voosen 2021, Korenaga 2021). Such a scenario has important implications for the emergence of dry land, which played a number of roles in mineral diversification, for example through the formation of minerals by evaporation, volcanic fumaroles, hot springs and geysers, photo-oxidation, lightning strikes, and impact mineralization. In spite of uncertainties regarding the extent of dry land, we assume that at least some subaerial continental crust has been present continuously since ~4.4 Ga. The nature of Earth's earliest atmosphere: That Earth's atmospheric composition has

The nature of Earth's earliest atmosphere: That Earth's atmospheric composition has changed dramatically through time is certain. However, the nature and timing of those changes is another enigmatic aspect of early Earth that influences models of Hadean mineral evolution. The widely cited model of Zahnle and colleagues (Zahnle 2006; Zahnle et al. 2007) suggests a Hadean transition from an initially dense CO₂-rich atmosphere to one dominated by N₂ – a change that must have been accompanied by extensive early deposition of carbonate minerals. We adopt this

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scenario and assume that carbonate precipitation was an important paragenetic process throughout the Hadean Eon. The nature and timing of the commencement of plate tectonics: The initiation of subduction, possibly tied to a transition from vertical (plume-dominated or "heat pipe") tectonics to modern-style lateral tectonics (Van Kranendonk et al. 2004, 2007a; Moore and Webb 2013), dramatically expanded Earth's mineralogical repertoire. However, significant uncertainties are reflected in a range of competing models regarding both the style and timing of extensive crustal recycling (Condie and Pease 2008; Brown et al. 2020; Korenaga 2021). Estimates for the initiation of plate tectonics range from > 4 Ga (Hopkins et al. 2008; Rosas and Korenaga 2018; Turner et al. 2020) to < 1 Ga (Stern 2005, 2018; Rollinson 2007a), with additional discussions related to continuous versus episodic processes (O'Neill et al. 2007; Belousova et al. 2010; Moyen and van Hunen 2012). In spite of these varied ideas, many researchers have concluded that a significant transition occurred near ~3 Ga to a "modern style" plate tectonics, exemplified by the Wilson cycle (Shirey and Richardson 2011; Dhuime et al. 2012; van Hunen and Moyen 2012; Tang et al. 2016; Cawood et al. 2018). In this study we assume that significant subductiondriven plate tectonics and associated mineral-forming processes began at some point after the earliest appearance of oceans and continental crust (i.e., < 4.3 Ga), but significantly before atmospheric oxygenation (> 3.0 Ga). In conclusion, we assume the following sequence of mineral-forming processes associated with the evolution of Earth's lithosphere and hydrosphere: (1) solidification of

a mafic/ultramafic crust (Stage 3a; > 4.50 Ga); (2) formation of oceans and an active

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hydrosphere (Stage 3b; > 4.45 Ga); (3) continental crust formation (Stage 4; > 4.40 Ga); and (4) initiation of subduction-driven plate tectonics (Stage 5; < 4.3 Ga). Note that this timeline is significantly more compressed than originally proposed by Hazen et al. (2008), thus suggesting that much of Earth's mineral diversity was established within the first 250 million years. Preservation bias: A critical factor impeding our understanding of the relative timing of paragenetic modes relates to inevitable biases associated with limited preservation of Archean and Proterozoic rocks, especially near-surface minerals associated with evaporites, fumaroles, hot springs, and other transient environments (e.g., Liu et al. 2019). Most minerals from those sources have been preferentially lost – preservation biases that are especially relevant to documenting the first appearance of many rare minerals (Hazen and Ausubel 2016). Therefore, the absolute and relative timing of Earth's earliest minerals must often be inferred from geochemical and geophysical models. Significant uncertainties in the timing of mineral paragenesis relate to the emergence of minerals incorporating rare elements. In particular, 41 relatively rare mineral-forming elements (defined here as present at < 5 ppm in Earth's crust), including Sb, As, Be, Bi, Br, Cd, Cs, Au, Hf, In, Hg, Mo, Se, Ag, Ta, Te, Tl, Sn, U, W, the platinum group elements, and the rare earth elements, account for almost 2400 mineral species. Thus, fewer than 1 in 10,000 crustal atoms play an essential role in more than 42 % of Earth's total mineral diversity (https://rruff.info/ima, accessed 7 March 2021). An unanswered

question is how much time is required for these scarce elements to achieve localized concentrations sufficient to produce new minerals.

Some evidence points to time periods greater than a billion years, as exemplified by the earliest known minerals containing Be (Grew and Hazen 2014), Cs (London 2008), and Hg (Hazen et al. 2012) from 3.00, 2.65, and 3.04 Ga, respectively. The paucity of these and other minerals containing rare elements with ages greater than 3 Ga suggests that it takes hundreds of millions of years for some scarce elements to become sufficiently concentrated, perhaps through fluid-rock interactions in large volumes of crust and upper mantle rocks affected by subduction-generated fluids.

On the other hand, at least some minerals incorporating rare elements arose much earlier in highly localized deposits, many of which did not survive or are yet to be exhumed. For example, micrometer-scale "nuggets" of PGE alloys enriched in osmium and ruthenium have been found in meteorites, formed > 4.55 Ga either as primary condensates from the solar nebula (Morrison and Hazen 2020) or exsolved from thermally metamorphosed Fe-Ni metal of differentiated planetesimals and preserved in iron meteorites (Hazen and Morrison 2021). Thus, in spite of the presence of Os and Ru at crustal concentrations of 1 part per billion or less, these platinum group elements rapidly segregated into concentrations sufficient to form PGE minerals. We conclude that much more research will be required to determine how rapidly minerals of rare elements might have formed in Earth's crust.

Systematic Survey of Paragenetic Modes

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In this section we describe 57 paragenetic modes of minerals, listed in a suggested order of earliest appearance, as summarized in Table 1. This analysis is based on a newly constructed database of 5659 minerals, each represented by one or more paragenetic modes (see Supplementary xlsx spreadsheet, [EDITOR: Please advise here on format]) – work that would not have been possible without the availability of large and growing open-access data resources (Hazen 2014; Lafuente et al. 2015; Hazen et al. 2019; Golden 2020; Prabhu et al. 2021). Paragenetic modes for each IMA-CNMNC-approved mineral species were determined by consulting one or more of the following sources: (1) lists of IMA-approved mineral species and associated links to primary references (https://rruff.info/ima, accessed 25 February 2021; Lafuente et al. 2015); (2) tabulations of mineral species and their localities, associated species, and (in many instances) geological contexts (https://mindat.org, accessed 25 February 2021); (3) detailed descriptions of paragenesis for rock-forming minerals in Deer et al. (1982-2013), Rock-Forming Minerals, Second Edition, 11 volumes; (4) brief descriptions of "Occurrence" in Anthony et al. (1990-2003), Handbook of Mineralogy, 6 volumes; and (5) books and articles describing new individual mineral species and their modes of occurrence from primary references (as listed in sources 1 through 4, above). This initial version of the paragenetic mode spreadsheet, with 10,556 combinations of an IMA-approved mineral species and one of 57 paragenetic modes, represents an ongoing effort; we welcome additions and corrections.

Several aspects of this treatment (Table 1) should be noted:

• While most of the paragenetic modes encompass numerous mineral species, several unusual categories are represented by 10 or fewer minerals. These relatively rare

paragenetic processes include minerals formed by interstellar condensation [#2] (8 species), near-surface freezing [#18] (4), auto-oxidation through radioactive decay [#27] (9), photo-oxidation [#28] (10), lightning [#29] (9), and shear stresses such as mylonitization [#43] (9).

• A significant number of durable mineral species, including metal alloys, carbides, and chalcogenides, are known only from detrital deposits, placers, or heavy mineral separates. In several instances, the origins of these grains are unknown. We list

"detrital" as a paragenetic mode, even though detrital refers to a local accumulation

of mineral grains in a sedimentary environment, as opposed to a formation

mechanism, per se.

- A number of mineral-forming processes, including exsolution, order-disorder transitions, and reversible phase transitions, occur in the solid-state during cooling and/or annealing. We have chosen to lump these processes with broader igneous and metamorphic paragenetic categories rather than treat them as separate formation processes. However, solid-state transition mechanisms could be added as one or more paragenetic modes in future studies.
- Several minerals form only in specific environmental contexts, for example in fluid inclusions [e.g., zabuyeite; Li₂(CO₃)], in caves [guanine; C₅H₃(NH₂)N₄O], or as epitaxial overgrowths [marsturite; NaCaMn₃Si₅O₁₄(OH)]. We catalog these minerals according to their petrogenetic settings, rather than by their environmental contexts.
- Similarly, we do not consider the formation processes of morphologically distinct minerals, such as lava phenocrysts, minerals that occur exclusively as nanophases

619 (e.g., protoenstatite; MgSiO₃), or minerals that display efflorescence, as distinct 620 paragenetic modes. 621 • Finally, we do not list minerals from the Moon or Mars. The comparative mineralogy 622 of extraterrestrial bodies will be treated in a separate contribution. 623 624 Stage 0. Pre-terrestrial "Ur-minerals" We tabulate 296 IMA-approved species as pre-625 terrestrial minerals on the basis of their occurrences in meteorites (Hazen and Morrison 626 2021; Rubin and Ma 2021). We divide these diverse phases, at least 97 of which are 627 known only from meteorites, into six sequential paragenetic modes ([#1] through [#6]), 628 representing the first three stages of mineral evolution. 629 [#1 - Stellar atmosphere condensates]: The earliest of these phases, dubbed "Ur-630 minerals" by Hazen et al. (2008), include 22 IMA-approved mineral species that formed 631 prior to the solar nebula in the expanding, cooling atmospheres of highly-evolved stars 632 (Zinner 2014; Nittler and Ciesla 2016; Hazen and Morrison 2020). Stellar minerals, 633 which are identified by their extreme isotopic anomalies as pre-solar grains, include the 634 most ancient condensed matter yet identified, with some individual stellar moissanite 635 (SiC) grains dated ~7 billion years old (Heck et al. 2020). Hazen and Morrison (2020) 636 catalogued these stellar minerals and further subdivided them into three probable sources 637 - AGB stars, classic novae, and core-collapse supernovae. Subsequent work by Boujibar 638 et al. (2021) employed cluster analysis on the isotopic attributes of thousands of stellar 639 moissanite grains to identify at least seven distinct SiC groups associated with variants of 640 these stellar types.

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[#2 – Interstellar condensates]: Morrison and Hazen (2020) listed an additional 8 probable interstellar condensed molecular C-H-O-N "ice" phases, which have been identified in so-called "cool" (T < 20 K), "dense" (P < 10⁻¹³ atm) molecular clouds by telescopic observations of absorption and emission spectra of interstellar molecules in radio, microwave, or infrared wavelengths (Greenberg 1991; Whittet 2003; Gibb et al. 2004). All of these condensed phases would have formed prior to the solar nebula (i.e., > 4.567 Ga). With the exception of water ice, these molecular solids are not currently recognized as minerals by the IMA-CNMNC. Stage 1. Primary nebular phases Stage 1 of Earth's mineral evolution, which occurred between 4.567 and 4.561 Ga, encompassed two mineral-forming processes. [#3 – Solar nebular condensates]: Initial mineral formation occurred as nebular gas cooled and highly refractory phases condensed at temperatures greater than ~1000 K. Morrison and Hazen (2020) catalogued 48 IMA-approved minerals that are preserved in calcium-aluminum-rich inclusions (CAIs; MacPherson 2014), amoeboid olivine aggregates (AOAs; Krot et al. 2004), and ultra-refractory inclusions (URIs; El Goresy et al. 2002). [#4 – Primary chondrule phases]: Overlapping pulses of nebular mineralization are preserved as the primary igneous minerals of chondrules, which represent solidified droplets, typically < 0.1 cm diameter, that formed during the first few million years of the solar nebula, ~4.566 to 4.561 Ga (Brearley & Jones 1998; Krot et al. 2014; Russell et al. 2018; Hazen et al. 2021). Chondrules are preserved in abundant chondrite meteorites, which may be thought of as the oldest sedimentary rocks in the solar system. We identify

664 47 primary chondrule minerals, most of which form from 10 abundant chemical elements 665 - C, O, Mg, Al, Si, S, Ca, Ti, Cr, and Fe. 666 Stage 2. Planetesimal differentiation Within the first million years of the solar nebula's 667 668 formation, the primary condensates of Stage 1 had begun to accrete into the first 669 generation of planetesimals. Over the next few million years (~4.566 to 4.560 Ga; 670 Blichert-Toft et al. 2010), some of these bodies grew to diameters exceeding 100 km – 671 large enough to melt and differentiate into a metallic core and rocky mantle. Subsequent 672 collisions disrupted some of these objects to produce a rich variety of non-chondritic 673 meteorites. 674 [#5 - Primary asteroid phases]: Morrison and Hazen (2021) tabulate 94 IMA-675 approved species that occur as primary igneous minerals in iron, stony-iron, and 676 achondrite meteorites (Mittlefehldt et al. 1998; Krot et al. 2014; Mittlefehldt 2014). 677 [#6 – Secondary asteroid phases]: A final pre-terrestrial phase of mineral evolution is 678 preserved as a diverse variety of secondary phases formed by aqueous, thermal, and/or 679 impact alteration of prior meteorite minerals. These processes produced more than 200 680 IMA-approved mineral species, primarily during an interval from ~4.565 to 4.550 Ga 681 (McSween et al. 1988; Brearley and Jones 1998; Mittlefehldt et al. 1998; Hazen and 682 Morrison 2021; Rubin and Ma 2021). This period of secondary mineralization saw the 683 first occurrence of several important mineral groups, including sulfates, carbonates, 684 hydroxides, and layer silicates (notably clay minerals). 685 An important caveat relates to the distinction between primary and secondary 686 meteorite minerals. Most secondary meteorite minerals are unambiguously the products 687 of aqueous and/or thermal alteration of earlier phases, yet at least two complications may

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arise. First, terrestrial weathering may lead to some secondary alteration that is difficult to distinguish from pre-terrestrial processes. However, most terrestrial weathering products arise from oxidation (see Stage 7 below) and are thus distinct from asteroidal alteration. A subtler situation arises from the gradual alteration of primary asteroid minerals to secondary phases. Such transformations may involve incremental shifts in composition and atomic structure spanning thousands to millions of years. Some suites of secondary mineral properties, such as exsolution, order/disorder, or zoning, are the consequences of thermal and/or aqueous alteration, but sharp boundaries may not exist between the primary and secondary forms of minerals. Furthermore, it has been suggested that some presumably secondary asteroidal minerals might have also formed via primary nebular processes, for example via sulfidization, oxidation, and/or hydration during preaccretionary interactions with a warm nebular gas (Krot et al. 1995, their Table 2; Bischoff 1998; Ciesla at al. 2003). These ambiguities are emblematic of challenges to any comprehensive tabulation of mineral paragenesis. Stage 3a. Earth's earliest Hadean crust Proto-Earth's earliest crust must have solidified before 4.55 Ga, shortly after the planet's accretion and differentiation, though that stage of Earth's mineral evolution is lost. The Moon-forming event (perhaps ~ 4.51 Ga; Barboni et al. 2017) completely obliterated the initial solid outer shell, but a new crust dominated by ultramafic and mafic igneous lithologies crystalized shortly thereafter (> 4.50 Ga). No minerals have been preserved from that Hadean world, save for a few detrital zircon (ZrSiO₄) crystals with ages as great as 4.4 Ga (Wilde et al. 2001).

711 Nevertheless, we suggest that five major groups of minerals, totaling approximately 400 712 mineral species, arose from this earliest terrestrial Stage 3a of mineral evolution (modes 713 [#7] through [#11]; Table 1). Many of these phases, previously cataloged by Hazen 714 (2013) and Morrison et al. (2018) in inventories of Hadean "paleomineralogy," are 715 familiar oxides and silicates with the most abundant crustal elements (notably H, Al, Na, 716 Mg, K, Ca, Fe, and Ti), as well as accessory sulfides, possibly arsenides, and other 717 relatively reduced phases. [#7 – Ultramafic igneous rocks]: Ultramafic igneous rocks, including peridotite, 718 719 pyroxenite, and komatiite, are dominated by ferromagnesian minerals and lack significant 720 plagioclase (Dick 1989; Isley and Abbott 1999; Guilbert and Park 2007; Philpotts and 721 Ague 2009; Lambert et al. 2016). These lithologies played a significant role in the 722 mineralogy of Hadean Earth's crust and mantle (Rollinson 2007b; Van Kranendonk et al. 723 2007b), though significant uncertainty remains regarding the relative volumes of 724 ultramafic versus mafic lithologies (e.g., Korenaga 2021). We list 123 minerals that have 725 been identified in ultramafic intrusive and extrusive igneous rocks. 726 [#8 - Mafic igneous rocks]: Mafic igneous rocks, notably volcanic basalt and its 727 intrusive equivalent gabbro, have been important crustal lithologies throughout Earth's 728 history (Rollinson 2007b; Van Kranendonk et al. 2007b; O'Neil et al. 2008). Most basalt 729 is thought to form by decompression partial melting of ultramafic rocks in Earth's 730 mantle, which produces a buoyant magma. Not only is basalt the dominant lithology of 731 the oceanic crust, but it also is produced in huge volumes in continental settings during 732 the episodic production of large igneous provinces (LIPS; Ernst 2014), which have 733 occurred since at least 2.8 Ga (Prokoph et al. 2004). The mineralogy of basalt is always

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dominated by plagioclase and pyroxene; however, a variety of basalt subtypes based on relative amounts of Mg, Fe, Al, Ti, and alkali metals incorporate different accessory minerals and display diagnostic compositional attributes. In this study, we identify 93 mineral species from Precambrian mafic igneous rocks. Further detailed studies of basalt minerals, for example employing cluster analysis on trace and minor elements, may point to additional subdivision of these phases into natural kinds (Hazen 2019; Boujibar et al. 2021). [#9 – Lava/xenolith minerals]: Additional mineralogical variety would have been present in the form of thermally-altered xenoliths that were derived from both mantle and crustal sources in abundant Hadean lavas (Grapes 2006). We identify 127 mineral species that were contributed by this igneous pyrometamorphic (most typically sanidinite facies) process. Note that some of these xenolith minerals, notably those representing altered carbonates and alkalic igneous rocks, must have formed significantly after 4.5 Ga to allow enough time for compositional differentiation. [#10 - Basalt-hosted zeolite minerals]: A significant number of late-stage zeolite group minerals likely formed in the cavities of cooling basalt (Deer et al. 2004). We identify more than 100 such phases, with the caveat that unaltered zeolite group minerals are rarely preserved in Precambrian formations and any tabulation based on ages of formation must remain speculative. [#11 – Volcanic fumarole minerals, reduced]: A modest suite of a few dozen reduced phases, predominantly transition metal sulfides, likely formed as sublimates at Hadean volcanic fumaroles (Grapes 2006; Vergasova and Filatov 2016). These phases represent a

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subset of the more than 450 documented fumarole minerals, most of which are more oxidized phases that we assign to post-GOE formation [#45].

Stage 3b. Earth's earliest hydrosphere Earth's earliest hydrosphere, fueled by ubiquitous volcanic venting of water vapor, led to cloud formation, rain, development of streams and rivers, and ultimately the establishment of oceans. A robust hydrological cycle was probably operating shortly after the solidification of Earth's crust, with substantial bodies of water covering a large fraction of the surface by > 4.45 Ga (Wilde et al. 2001; Elkins-Tanton 2011; Dong et al. 2021), and a vigorous subsurface hydrothermal circulation of aqueous fluids (Heinrich and Henley 1989; Pirajno 2009). The consequent water-rock interactions may have produced as many as 350 mineral phases in nearsurface marine and terrestrial environments. [#12 – Hadean hydrothermal minerals]: Subsurface Hadean hydrothermal sulfide deposits, with more than 100 likely species, represent an important yet enigmatic early source of mineral diversity. Today, hydrothermal systems boast more than 850 species of sulfides, arsenides, antimonides, and a wide range of sulfosalts bearing relatively rare elements such as Ge, Sn, Bi, Se, and Te. However, we postulate that these uncommon elements were not sufficiently concentrated in Hadean hydrothermal fluids to generate that wide range of compounds. In spite of longstanding interest in the secular variation of sulfide-rich ore bodies (Laznicka 1973; Meyer 1988; Titley 1993; Barnes and Rose 1998; Goldfarb et al. 2001; Groves et al. 2005, 2010; Huston et al. 2010; Leach et al. 2010; Maier and Groves 2011; Jenkin et al. 2015), the changing mineralogies of these deposits

through time, especially regarding minerals containing relatively rare elements, have not

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been detailed to our knowledge. We therefore limit our list of the earliest hydrothermal chalcogenides to sulfides (and in a few cases arsenides) of the commonest transition metal elements, as well as PGE elements, which are thought to concentrate in fluids associated with ultramafic lithologies owing to their highly incompatible nature (Mungall and Naldrett 2008). We list most hydrothermal ore minerals under Stage 4 [#33], when extensive fluid-rock interactions in the upper mantle and crust associated with subduction is thought to have selected and concentrated rare elements. [#13 – Hadean serpentinization]: Low-temperature aqueous alteration of Hadean igneous lithologies, in both near-surface and subaerial environments, must have produced hundreds of new mineral species. Most notably, serpentinization would have transformed ocean floor mafic and ultramafic rocks to familiar assemblages of brucite, serpentine, magnetite, and more than 60 other phases (Blais and Aubrey 1990; Lowell and Rona 2002; Palandri and Reed 2004; Shrenk et al. 2013; Holm et al. 2015; Menez et al. 2018). [#14 - Hot springs, geysers]: The surface of the Hadean world would have featured abundant subaerial hot springs and geysers that produced a range of geothermal minerals, perhaps including the earliest terrestrial occurrences of calcite (CaCO₃), baryte (BaSO₄), and a variety of hydrated phases. 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). [#15 – Black/white smokers]: A subset of more than 20 hydrothermal sulfide minerals would have occurred with high-temperature aqueous alteration phases at Earth's earliest "black smoker" environments, which, along with carbonate-rich "white smokers," we consider to be a distinct seafloor paragenetic environment (Hekinian et al. 1980; Haymon

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and Kastner 1981; Palandri and Reed 2004; Schwarzenbach and Steele-MacInnis 2020). Note that the abundance and character of submarine hydrothermal vents may have changed significantly through time. Compared to today, Hadean Earth had significantly greater volcanic activity coupled with a larger extent of oceans. Nevertheless, the onset of modern-style plate tectonics would have established continuous chains of submarine vents at and near divergent plate boundaries (Lowell et al. 2008). Therefore, we conclude that seafloor hydrothermal systems have been active mineral-forming environments for at least 4.5 billion years. [#16 - Low-T aqueous alteration]: In addition to serpentinization, low-temperature aqueous alteration of Hadean subaerial and shallow subsurface lithologies produced more than 80 mineral species, including dozens of zeolites, clay minerals, and other hydrous silicates (Deer et al. 2004; Wilson 2013). [#17 – Marine authigenic minerals]: Hadean seafloor water-rock interactions would have produced a complementary suite of perhaps 50 authigenic phases in lowtemperature marine sediments, including a variety of hydrous silicates, notably zeolites (Deer et al. 2004). We have attempted to differentiate authigenic minerals, which precipitated in place (typically in a sedimentary environment), from aqueous processes that alter prior minerals through fluid-rock interactions (e.g., modes [#16], [#22], [#23], [#46], and [#47]). Note also that we distinguish these marine authigenic minerals, which began forming early in the Hadean Eon, from those that we suggest formed somewhat later in a continental setting [#24]. [#18 – Minerals formed by freezing]: Finally, the Hadean hydrosphere must have hosted the earliest terrestrial examples of minerals formed by freezing of aqueous

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solutions, most abundantly ice (H₂O), but also rare occurrences of hydrohalite (NaCl'2H₂O), ikaite (CaCO₃'6H₂O), and possibly ernstburkeite [Mg(CH₃SO₃)₂'12H₂O], which was discovered in an ice core from Antarctica (Genceli Güner et al. 2013). Stage 4a. Earth's earliest continental crust The occurrence of individual zircon grains with ages as great as ~4.4 Ga (Wilde et al. 2001; Cawood et al. 2013) suggests that some granitic continental crust formed through partial melting of hydrated basalt within Earth's first 150 million years, significantly before the onset of modern-style plate tectonics according to many models (Shirey and Richardson 2011; Dhuime et al. 2012; van Hunen and Moyen 2012; Tang et al. 2016; Johnson et al. 2017; Cawood et al. 2018; however, see Korenaga 2021). Crustal processes during the Hadean and Archean Eons led to significant mineral diversification, ultimately approaching a total of 2400 mineral species (Table 1). [#19 - Granitic intrusive rocks]: We list 143 primary minerals that were associated with the formation of granite and related intrusive acidic rocks during the Hadean Eon – mineralization that continues today. Studies of many granitic bodies point to different sources of parent magmas, including mantle-derived ("M" type); sediment-derived ("S" type); deep-crustal, orogenic igneous ("I" type); and anorogenic ("A" type) granites associated with hot spots (Chappell and White 2001; Eiler 2007; Philpotts and Ague 2009). Therefore, an intriguing aspect of granite mineralogy, yet to be explored, is whether different types of granite might result in distinctive mineral attributes and thus warrant further paragenetic subdivisions.

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[#20 – Acidic volcanic rocks]: Rhyolite, dacite, and other quartz- and alkali feldsparbearing volcanic rocks played an important role in the evolution of continental crust (Rollinson 2007b; Van Kranendonk et al. 2007b; Philpotts and Ague 2009). We identify 45 mineral species produced by acidic volcanism, including phases uniquely associated with ash, such as quadridavyne [(Na,K)6Cl2Ca2Cl2(Si6Al6O24)], as well as its rapid devitrification and hydration products [e.g., clinoptilolite-Na; Na₆(Si₃₀Al₆)O₇₂ 20H₂O]. Note that we distinguish intrusive and extrusive acidic rocks because they have different suites of minerals, as opposed to ultramafic [#7] and mafic [#8] igneous rocks. [#21 – Chemical precipitates]: A wide variety of near-surface processes accompanied the establishment of subaerial continental and shallow marine environments, resulting in the formation of more than 1100 mineral species. Continental margins and lake environments saw significant chemical precipitation of carbonates (Falkowski et al. 2000; Boggs 2006), phosphorites (Baturin and Bezrukov 1979; Button 1982; Delaney 1998), and iron formations (Klein 2005; Bekker et al. 2010), with at least 79 associated mineral species. Extensive abiotic carbonate formations were especially consequential for environmental changes in the Hadean Eon, as they rapidly became the dominant crustal carbon reservoir, mirrored by a dramatic reduction of atmospheric CO₂ (Falkowski et al. 2000). [#22 – Low-T aqueous alteration]: Hydration and low-temperature aqueous alteration of a wide range of lithologies in shallow subsurface environments must have occurred as soon as surface rocks were exposed to water. We estimate that Hadean aqueous alteration led to 247 mineral species, including numerous hydrous silicates, hydrated phosphates in 869 altered granitic rocks, and more than 50 altered Mn minerals (Savage et al. 1987; Post 870 1999; Nishimoto and Yoshida 2010). 871 [#23 – Subaerial aqueous alteration]: We record an additional 398 minerals formed 872 by subaerial and near-surface aqueous alteration prior to significant oxidation (i.e., > 3 873 Ga). Many of these phases, notably including hydrous silicates, carbonates, phosphates, 874 and borates, likely form today in relatively reducing environments (Chang et al. 1996). 875 This suite of several hundred mineral species contrasts with the almost 2000 876 oxidized/weathered species that appeared following the GOE (< 3 Ga) [#47]. 877 [#24 – Terrestrial authigenic minerals]: We identify 74 minerals that likely formed in 878 continental sediments as authigenic species, in contrast to marine authigenic phases 879 [#17]. Most of these minerals are relatively common silicates, carbonates, or phosphates that are known to form in a variety of environments (Chang et al 1996; Deer et al. 2006). 880 881 [#25 – Evaporites]: The emergence of dry continental crust, with the likely occurrence 882 of extensive inland seas, saw increased opportunities for deposition of diverse evaporite 883 minerals (Button 1982; Buick and Dunlop 1990). We catalog 210 plausible phases; 884 however, the relative chronology of their first appearances, which must have been 885 strongly tied to composition, is not known. Halides, notably halite (NaCl) and sylvite 886 (KCl), must have formed on Earth's first shorelines in the early Hadean Eon. Sulfates 887 may have followed soon thereafter, especially if abiotic sulfur photo-oxidation played a 888 significant role in near-surface processes (see mode [#28] below). However, it may have 889 taken much longer for significant deposition of borates or nitrates to occur (e.g., Grew et 890 al. 2011, 2015).

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[#26 – Detrital minerals]: Numerous mechanically robust minerals, including dozens of metal alloys, carbides, and chalcogenides not yet discovered in situ, are preserved in sediments as detrital minerals (Baker 1962). We list 250 detrital mineral species that we suggest were present by the Hadean or Archean Eons. We have attempted to assign most of these phases to other paragenetic modes, as well, based on their chemistries and assumed lithological associations. Note, however, that in a few instances the original contexts of detrital minerals are unknown [e.g., enigmatic tantalcarbide (TaC) and niobocarbide (NbC)]; therefore, in these few examples the true paragenetic mode is unresolved. [#27 – Radioactive processes]: A number of minor but intriguing paragenetic processes led to the formation of idiosyncratic minerals in near-surface environments. For example, primary uranium minerals of the Hadean Eon would have invariably formed as phases, most commonly uraninite (UO2) and coffinite (USiO4). However, radioactive decay of U⁴⁺ to Pb²⁺ led to the intriguing phenomenon of "auto-oxidation," by which uranium is oxidized to U⁶⁺ (Frondel 1958; Finch and Murakami 1999; Hazen et al. 2009, and references therein). Auto-oxidation resulted in localized formation of a few uranyl-oxide-hydroxide phases, notably ianthinite [U⁴⁺(U⁶⁺O₂)O₄(OH)₆(H₂O)₉]. schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}]$, and becquerelite $[Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8]$, as well as Pb-bearing phases such as fourmarierite [Pb[(UO₂)₄O₃(OH)₄](H₂O)₄], kasolite [Pb[(UO₂)(SiO₄)](H₂O)],vandendriesscheite and $[Pb_{1.5}[(UO_{2})_{10}O_{6}(OH)_{11}](H_{2}O)_{11}].$

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[#28 – Photo-alteration]: Early Earth did not have a protective ozone layer; therefore, the near-surface environment was highly susceptible to UV photo-oxidation – a potentially widespread but as yet incompletely studied phenomenon. A limited number of minerals are known from laboratory studies to form by photo-oxidation processes (e.g., Kim et al. 2013); we list 10 of these species. In some instances, such as pararealgar (AsS), digenite (Cu_{1 8}S), and ramsdellite (MnO₂), new minerals are known to form from prior minerals that are exposed to visible light or ultraviolet radiation. Less well studied are processes by which UV oxidation produces reactive oxidized chemicals, notably the conversion of aqueous Fe²⁺ to Fe³⁺ with associated reduction of water and release of H₂. Recent experiments by Yee and colleagues (Nathan Yee, personal communication, 7 February 2021) reveal that Fe³⁺ is a strong oxidant that can lead, for example, to abiotic production of elemental selenium and sulfate minerals from primary selenides and sulfides in anoxic environments. One can infer that many analogous reactions might have occurred during the Hadean and early Archean Eons, for example producing a suite of arsenate and antimonate minerals from precursor arsenides and antimonides. We are not yet able to definitively catalog such prebiotic oxidized phases; however, the possibility remains that significant mineral diversity arose indirectly through photo-oxidation prior to the Great Oxidation Event (*Stage 7*). [#29 – Lightning minerals]: A small suite of 9 highly-reduced minerals, including silicon metal, graphite, iron, moissanite, and schreibersite, is associated with the production of fulgurites by lightning strikes (Essene and Fisher 1986; Grapes 2006; Pasek et al. 2012; Hess et al. 2021). Pasek and Block (2009) suggested that lightning-induced

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reduction of phosphate minerals might have provided a source of biologically useful P compounds prior to life's origins – an idea amplified by Hess et al. (2021). [#30 – Terrestrial impact minerals]: Bolide impacts on exposed Hadean crust must have produced a range of high-pressure shock-induced phases. We tabulate 16 known impact species, including high-pressure forms of carbon (diamond), SiO2 (coesite, stishovite, and chaoite), TiO₂ (riesite and akaogiite), and other oxides and silicates (Tomioka and Miyahara 2017; Tschauner 2019). [#31 – Thermal alteration] Thermal metamorphism of diverse lithologies, including sediments, igneous rocks, and metal-rich deposits, led to more than 1500 new phases produced in subsurface continental environments. We tabulate 356 minerals that were produced by thermal alteration reactions of prior phases with aqueous fluids, notably those rich in carbonate and phosphate, as well as sulfate, borate, halogens, and other solutes. Continents with deep roots and active hydrological cycles also hosted mineral formation in more extreme subsurface environments, for example by high-temperature alteration through metasomatism and/or contact metamorphism of carbonates (Falkowski et al. 2000), phosphates (Button 1982), and iron formations (Klein 2005; Kappler et al. 2005). [#32 – Ba/Mn/Pb/Zn deposits]: A remarkable variety of high-temperature minerals containing Ba, Mn, Pb, and/or Zn, including contact and regional metamorphic deposits, arose through processes in the continental crust (Post 1999; Leach et al. 2010). We tabulate 412 species, including 185 phases unique to these environments, from classic localities, including the Wessel manganese mine, South Africa (Caincross and Beukes 2013); Broken Hill, Australia (Spry et al. 2008); Fresno County, California (Alfors et al.

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1965); and Franklin, Sussex County, New Jersey (Peters et al. 1983). These occurrences underscore the importance of a few mineral-rich localities in establishing Earth's mineral diversity. [#33 – Hydrothermal deposits]: Subsurface hydrothermal deposition of metal-rich veins and other bodies, primarily in environments associated with volcanism, produced ~ 800 mineral species, most of which are unique to hydrothermal origins. Significant uncertainties remain regarding the sequence and timing of the earliest appearances of these varied, economically important sulfide, arsenide, selenide, antimonide, and related sulfosalt minerals (Meyer 1988; Guilbert and Park 2007; Bradley 2011). We suggest that early Hadean formations contained a relatively small subset of these phases, primarily sulfides and some arsenides of the commoner transition elements; accordingly, we list 129 mineral species associated with mode [#12]. Note that prior to enhanced mineralization associated with plate tectonics (Hazen et al. 2014; Groves et al. 2015), most volcanism was likely associated with hot spots and vertical tectonics – processes that may have been accompanied by far less crustal fluid-rock interactions than today's subduction-related volcanism. We suggest that relatively few large-scale, metal-rich hydrothermal systems would have occurred in those settings, analogous to what is observed today at mineral-poor hot spots such as Hawaii, Yellowstone, and Iceland (Sherman et al. 1968; Plazo-Toledo 2019). We conclude that the advent of subductionrelated volcanism, the appearance of volcano-hosted massive sulfide deposits, and the associated concentrations of relatively rare elements were essential for the dramatic expansion of hydrothermal mineral diversity.

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Stage 4b. Highly evolved igneous rocks Significant mineral diversity is associated with the concentration of rare, incompatible elements in late-stage magmas. "Complex" granitic pegmatites, agpaitic and miaskitic pegmatites, carbonatites and related carbonrich magmas, and layered igneous intrusions with concentrations of PGE elements account for 1476 mineral species, 662 of them unique to those compositionally idiosyncratic environments. All of these lithologies were present by the end of the Archean Eon; however, the timing of the most ancient of these formations is uncertain, as their relative rarity, coupled with erosional loss, results in an imperfect record. [#34 – Complex granite pegmatites]: We tabulate 564 mineral species that are found in granite pegmatites, with 238 rare species known only from that environment. The earliest documented occurrences of pegmatite minerals with essential Li and Be are from Mesoarchean formations (\sim 3.1 to 3.0 Ga), including the Barberton greenstone belt, South Africa, and the Zishineni pegmatite, Swaziland (Tkachev 2011; Grew et al. 2017, 2019), while the oldest known complex pegmatite with Cs mineralization is the 2.64 Ga Tanco Mine in Manitoba, Canada (Černý 2005; London 2008). These earliest known examples of complex granitic pegmatites may reflect the extreme concentration of rare elements that was facilitated by subduction and consequent fluid-rock interactions in large volumes of the crust and upper mantle, and thus only possible < 3 Ga. [#35 – Ultra-alkali rocks]: Pegmatites from ultra-alkaline agpaitic and miaskitic rocks display even greater mineral diversity than granite pegmatites, with 726 recorded species (Marks and Markl 2017; Mikhailova et al. 2019), including 377 minerals that are unique to agpaitic formations. Much of this mineralogical diversity results from the unusual

1002 concentration of Be, Ti, Y, Zr, Nb, and rare earth elements in these alkali-rich, silica-poor 1003 rocks. 1004 [#36 - Carbonatites]: Carbonatites, kimberlites, and related carbonate-bearing igneous 1005 rocks (Mitchell 1986; Jones et al. 2013) hold 291 distinctive minerals, including dozens 1006 of rare carbonate and phosphate species. These intriguing lithologies have been present 1007 since at least the Mesoarchean Era. Among the oldest known occurrences are the 3.01 Ga 1008 Tupertalik carbonatite from Greenland (Downes et al. 2012), and the 2.6 Ga Siilinjarvi 1009 carbonatite from Finland (Patchett et al. 1982; Woolley and Kjarsgaard 2008), whereas 1010 the Ol Doinyo Lengai volcano in Tanzania continues to erupt low-viscosity carbonate 1011 lavas. 1012 [#37 – Layered igneous intrusions]: In spite of their affinity to other mafic/ultramafic 1013 igneous rocks, we consider layered igneous intrusions to be a separate paragenetic 1014 environment because of their unusual homogeneous aerial extent, their predominantly 1015 Precambrian ages, and the common occurrence of metal-enriched layers with more than 1016 100 PGE and Cr-Ti-Fe oxide mineral species, including a number of phases reported 1017 from no other source (Naldrett et al. 1987; Maier and Groves 2011; Zientek 2012; 1018 O'Driscoll and VanTongeren 2017). The oldest known PGE deposit is the 3.2 Ga Baula 1019 deposit in India (Augé et al. 1993), with several Neoarchean and Paleoproterozoic 1020 examples recorded from localities in Africa and North America (Maier and Groves 1021 2011). 1022 1023 Stage 5. Initiation of plate tectonics Crustal recycling via plate tectonics was a 1024 significant driver of mineral diversification, largely as a consequence of mineralization

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associated with orogenesis, as well as the first subaerial exposure of otherwise hidden high-P-T lithologies. We adopt the prevailing view that modern-style, subduction-driven plate tectonics was well established prior to 3 Ga, as manifest in the Wilson cycle and episodes of supercontinent assembly (Huston et al. 2010; Nance et al. 2014; Hazen et al. 2014), with significant earlier crustal recycling perhaps before 4 Ga (e.g., Condie and Pease 2008; Korenaga 2021). [#38 – Ophiolites]: The stranding of ophiolites, which are highly altered sequences of mafic and ultramafic rocks from the deep oceanic lithosphere, provides an important glimpse of the mineralogy and petrology of the crust-mantle boundary (Moores 2002; Dilek 2003; Kusky 2004). Ophiolites, which hold at least 108 mineral species, are in many respects similar to ocean floor rocks altered by serpentinization. However, their unique subaerial settings and exposures of mantle lithologies warrants a separate paragenetic category. Furthermore, the mineralogically unique Luobusha ophiolite from the Shannan Prefecture of Tibet is of special interest for a remarkable suite of dozens of UHP (e.g., diamond and moissanite) and highly-reduced phases, including native elements (Al, Cr, Cu, Fe, Ti, W), carbides, nitrides, and phosphides (Bai et al. 2011). In addition, the Luobusha occurrence features many PGE metal alloys (including approximately 30 as yet undescribed metal phases), in association with chromitite zones that are reminiscent of assemblages in layered intrusions [#37]. We include these diverse, rare minerals under ophiolites, though details of their paragenesis remain obscure. Debates persist regarding the oldest ophiolite. Furnes et al. (2007) suggested that an altered dike complex in Greenland's 3.8 Ga Isua supracrustal belt represents a "vestige" of oceanic crust, though this interpretation was questioned by Nutman and Friend (2007).

1048 The next oldest claim, the 2.5 Ga Dongwanzi ophiolite complex from China (Kusky et al. 1049 2001) has also been debated (Zhai et al. 2002; Kusky and Zhai 2012); however, 1050 descriptions of several altered Neoarchean examples support an origin by at least 2.5 Ga 1051 (Kusky 2004), providing further evidence that plate tectonics was well established in the 1052 late Archean Eon. 1053 [#39 – High-P metamorphism]: Plate tectonic processes have also led to the exposure 1054 of metamorphic rocks from environments with unusually low geothermal gradients, 1055 estimated to be < 10 °C/km – conditions only possible during relatively rapid subduction 1056 of crustal rocks to great depths, with subsequent buoyant uplift (Chopin 1984; Hacker 1057 2006; Palin and White 2016; Zheng and Chen 2017). These rocks include blueschist 1058 facies with glaucophane, jadeite, and/or lawsonite (formed at depths to 30 km); eclogite 1059 with pyrope and omphacite (> 45 km); and so-called "ultra-high pressure" (UHP) 1060 formations, featuring the dense coesite form of SiO₂ (> 80 km). The oldest known 1061 examples of these high-pressure lithologies are from the Neoarchean Era (~2.8 Ga), 1062 which coincides with models of plate tectonics commencing at ~3 Ga (Jahn et al. 2001; 1063 Brown 2007). We list 70 associated minerals, of which a dozen species, including 1064 trinepheline (NaAlSiO₄), kokchetavite (KAlSi₃O₈), and barioperovskite (BaTiO₃), are 1065 unique to these high-pressure metamorphic rocks. 1066 [#40 - Regional metamorphism]: Regional metamorphism associated with burial, 1067 alteration, and uplift of thick accumulations of sediments, volcanic rocks, and intrusive 1068 igneous rocks led to 319 mineral species. Most regional metamorphic rocks formed at 1069 depth under an average geothermal gradient of > 15 °C/km to ~30 °C/km (Vernon 2008; 1070 Philpotts & Ague 2009). These rocks are usually subdivided into facies based on the

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appearance of new minerals with increasing P and T: greenschist (typically with chlorite, serpentine, and epidote), amphibolite (amphibole and plagioclase), and granulite (pyroxene and plagioclase). We lump all of these regional metamorphic facies in this study, while acknowledging that further subdivision of metamorphic lithologies may be warranted in future studies. [#41 – Mantle metasomatism]: Mantle metasomatism (Luth 2003; O'Reilly and Griffin 2012) is a high-pressure hydrothermal metamorphic process that alters the chemistry of existing ultramafic minerals and produces new phases through interactions with deep C-O-H fluids (Manning and Frezzotti 2020). We identify 16 oxide and silicate mineral species formed through mantle metasomatism, all but 1 of which (nixonite, Na₂Ti₆O₁₃; Anzolini et al. 2019) are well known from other environments. [#42 – Seafloor nodules]: Seafloor nodules are enigmatic Mn- and Fe-rich concretions with significant Ni, Cu, and Co content that form extensive (and potentially economic) deposits on some regions of the ocean floor. While these nodules may be authigenic and thus a subset of mode [#17], their mineralogy and morphology appear to be distinct. If, as some contend, they form through microbial mineralization (Lysyuk 2008; Blöthe et al. 2015) or through precipitation in an oxic environment (Fike et al. 2006; Wegorzewski and Kuhn 2014), then this paragenetic category should be moved to Stage 6 or Stage 7. If, on the other hand, they form by the release and reprecipitation of metals from ultramafic rocks and/or from hydrothermal vents (Hlawatsch et al. 2002), then metal-rich nodules may have appeared as early as Stage 3 or Stage 4. We provisionally assign seafloor nodules to Stage 5, based on the assumption that Mn release increased at 1093 spreading centers following the crustal recycling of plate tectonics. We list 15 minerals 1094 from Mn nodules, 11 of which are Mn or Fe oxides/hydroxides. 1095 [#43 – Shear-induced minerals]: Minerals produced by significant shear strain 1096 represent a distinct paragenetic mode, most commonly associated with polished fault 1097 surfaces known as slickensides (Passchier and Trouw 2005; Trouw et al. 2009). The closely related term "mylonite" relates to an altered zone of minerals recrystallized 1098 1099 through shearing. We list 9 minerals produced in shear zones, 8 of which are common 1100 oxides and silicates, that are reported to form anew in silicate rocks through this process. 1101 It is difficult to assess when shear-generated minerals first occurred. We associate them 1102 primarily with plate tectonic processes, but some examples must have occurred as early 1103 as the Hadean Eon. On the other hand, of special interest is the rare chlorite group 1104 mineral, donbassite [Al₂(Si₃Al)O₁₀(OH)₂·Al_{2,33}(OH)₆], which has been reported from 1105 slickensides of coal (Anthony et al. 1990-2003), and therefore must have formed at < 350 1106 Ma. 1107 1108 Stage 6. Anoxic biosphere [#44]: The rise of microbial life ~4.0 billion years ago appears 1109 to have had little initial impact on mineral diversity. However, some microbes learned to 1110 exploit minerals, using carbonates and phosphates as sturdy stromatolitic habitats 1111 (Chauhan 1979; Burnett and Riggs 1990; Cook and Shergold 1990; Grotzinger and Knoll 1112 1999; Van Kranendonk et al. 2003), as well as employing iron (and possibly other 1113 transition metal) oxide and sulfide phases as reliable sources of redox energy (Lowell et 1114 al. 2009; Ishibashi et al. 2015). We propose a conservative list of 11 microbially-1115 mediated minerals, all of them common phases found in five or more paragenetic

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environments, that are thought to have formed in anoxic environments prior to the rise of atmosphere that characterized Stage 7. Numerous instances of Archean minerals precipitated through microbial action have been documented (Grotzinger and Knoll 1999; Konhauser et al. 2002; Frankel and Bazylinski 2003; Schulz and Schulz 2005; Southam and Saunders 2005; Lepot et al. 2008). Unambiguous occurrences of microbial carbonate stromatolites occur as early as 3.5 Ga in rocks of the Pilbara craton in Western Australia (Van Kranendonk et al. 2003; Allwood et al. 2006), pointing to calcite, dolomite, and siderite as likely early biominerals. Similarly, biogenic phosphatic stromatolites (Banerjee 1971; Schulz and Schulz 2005) and iron formations (Anbar and Holland 1992; Akai et al. 1999) have been described from multiple localities as early as the Neoarchean Era. Stage 7. Great Oxidation Event The single most significant factor in Earth's mineral diversification was the Neoarchean/Paleoproterozoic rise of atmospheric oxygen, which we estimate led to the introduction of more than 2300 new mineral species. However, at least two significant uncertainties relate to the timing and nature of the formation of Earth's diverse oxidized mineral species. A persistent question relates to the timing of atmospheric oxygenation (Canfield 2014; Lyons et al. 2014). A number of early Earth scenarios point to the Great Oxidation Event as a prolonged period of atmospheric change, often modeled as occurring after 2.4 Ga, when global-scale oxygenic photosynthesis became well established. Important evidence for this change in atmospheric composition is found in the sulfur isotope record, notably in the disappearance of mass-independent S isotope fractionation in near-surface sulfur-

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bearing minerals (Farquhar et al. 2000, 2001, 2007). This rather abrupt change in the character of S isotope ratios is thought to have occurred owing to formation of a UVblocking ozone layer. However, other researchers point to intervals or oases of elevated atmospheric oxygen as early as 3.1 Ga based on pulses of redox-sensitive trace elements in Archean sediments (e.g., Anbar et al. 2007), as well as the postulated early appearance of microbial oxygen-utilizing enzymes (Jabłońska and Tawfik 2021). Those results suggest that a subset of oxidized mineral species might have formed prior to 2.4 Ga, during the Neoarchean Era. A second uncertainty relates to the extent of Archean abiotic processes that might have produced relatively oxidized mineral species. In particular, as noted above (see [#28]), UV-photooxidation of Fe²⁺ to Fe³⁺, followed by production of sulfates and other relatively oxidized minerals, may have been a ubiquitous process in near-surface waters prior to the establishment of a UV-blocking ozone layer. If this UV-mediated process was commonplace prior to the rise of atmospheric oxygen, then some of the relatively oxidized phases we ascribed to post-GOE biological O2 production may have emerged much earlier through abiotic chemistry. With those caveats in mind, we consider three important mineral-forming environments that were strongly influenced by atmospheric oxygenation. [#45 - Volcanic fumarole minerals, oxidized]: Volcanic fumaroles produce a remarkable variety of more than 420 relatively oxidized mineral species, 168 of which are unique to volcanic vents. We suggest that these minerals could only have been precipitated after the GOE (e.g., Vergasova and Filatov 2016). Accordingly, we tabulate 253 fumarolic sulfates, arsenates, selenates, and antimonates, as well as 171 other vent 1162 minerals, including carbonates, borates, nitrates, phosphates, and other phases 1163 incorporating a range of transition metals (V, Cr, Zn, Mo, W), halogens, and ammonia. 1164 We include intriguing pneumatolytic minerals [e.g., itelmenite, Na₂CuMg₂(SO₄)₄; 1165 Nazarchuk et al. 2018] that are thought to form by reactions of prior minerals with 1166 fumarolic gases (Krivovichev et al. 2013). 1167 [#46 – Oxidized hydrothermal minerals]: The formation of more than 2000 secondary 1168 minerals by near-surface "weathering," primarily oxidation and hydration, is by far the 1169 greatest single contributor to Earth's mineral diversity. The majority of these minerals 1170 form in direct contact with the oxygenated atmosphere (see [#47]). However, we 1171 distinguish 52 oxidized secondary minerals, primarily sulfates and arsenates, that are 1172 described as forming in hydrothermal environments. Thus, for example, mansfieldite 1173 [AlAsO₄'2H₂O] is reported by Anthony et al. (2003) to be "a hydrothermal product in altered and mineralized andesitic pyroclastic rocks" (and thus included in [#46]), in 1174 contrast to its Fe-bearing isomorph scorodite [Fe³⁺AsO₄·2H₂O], which is described as "a 1175 1176 secondary mineral formed by oxidation of As-bearing sulfides" and therefore assigned to 1177 [#47]. Similarly, cesanite [Ca2Na3[(OH)(SO4)3] (Cavarretta et al. 1981) and grandaite [Sr₂Al(AsO₄)₂(OH)] (Cámara et al. 2014) are described as hydrothermal minerals, 1178 1179 whereas compositionally similar antofagastaite [Na₂Ca(SO₄)₂·1.5H₂O] (Pekov et al. 1180 2019) and arsenogoyazite [SrAl₃(AsO₄)(AsO₃OH)(OH)₆] (Walenta and Dunn 1984) are 1181 presented as secondary oxidized phases. We have adopted the reported paragenetic 1182 modes of these oxidized minerals – hydrothermal versus secondary – while recognizing

1183 that a continuum exists for secondary oxidized minerals formed in near-surface 1184 environments. 1185 [#47 – Oxidative weathering]: We catalog 1998 secondary minerals formed in lowtemperature weathering environments in contact with a post-GOE oxygenated 1186 1187 atmosphere. Given this large number of secondary, oxidized minerals (35 % of all IMA-1188 approved species), we subdivide these phases into 9 overlapping compositional groups. 1189 Near-surface hydration of prior minerals is the largest subset, with 1649 species (82.5 % 1190 of [#47]). Other subsets include sulfates and sulfites (409 species); carbonates, 1191 phosphates, borates, and nitrates (577); arsenates, antimonates, selenates, and bismuthinates (505); vanadates, chromates, and manganates (372); uranyl (U⁶⁺) minerals 1192 1193 (236); and halogen-bearing minerals (236). A significant subset (316 species) of these 1194 weathering products are dehydrated, which may point to multiple stages of subaerial 1195 weathering that included both hydration and dehydration reactions. Finally, we include 1196 28 minerals known to form through the terrestrial weathering of meteorites [#47i], 1197 including 10 Fe, Ni, and/or Cr phases only known from the alteration of iron meteorites 1198 (Rubin and Ma 2021). 1199 An intriguing finding is that 1119 of these minerals – 20 % of Earth's total mineral 1200 diversity – are known to form only through paragenetic mode [#47]. These species 1201 formed exclusively by oxidative weathering are not equally divided among the 9 1202 compositional groups (Table 1). Approximately 45 % of sulfates and 51 % of halogen-1203 bearing phases in [#47] are only known as weathering phases, whereas 73 % of uranyl 1204 minerals are uniquely found in those near-surface oxidized environments. 1205

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Stage 8. Intermediate Ocean A billion years of the Proterozoic Eon (~1.8 to 0.8 Ga) was evidently a period of gradual oxygenation of the "intermediate ocean" (Anbar and Knoll 2002), coupled with reduced mineralization (Hazen et al. 2008; Bradley 2011; Hazen et al. 2014; Liu et al. 2019). Sometimes called the "boring billion" (Brasier 1998, 2012; Buick et al. 1995), this extended Proterozoic interval appears to have seen no new paragenetic processes. Stage 9. Snowball Earth The end of the Neoproterozoic Era (~0.8 to 0.6 Ga) featured at least three major episodes of global glaciation, when ice was the dominant mineral over most of Earth's surface from poles to Equator (Kirschvink 1992; Hoffman et al. 1998). Each of these "snowball Earth" events saw the cessation of significant continental weathering, while atmospheric carbon dioxide increased through the contributions of continuous volcanic emissions - changes that in turn led to an exaggerated greenhouse effect, global warming, and episodes of relatively rapid loss of ice cover. These intervening "hothouse Earth" periods must have seen enhanced surface weathering, notably accompanied by carbonate formation. However, no new paragenetic processes are associated with Stage 9 of mineral evolution. Stage 10a. Neoproterozoic oxygenation and the Phanerozoic biosphere The Phanerozoic Eon (< 541 Ma) has been characterized by significant mineralogical novelty, with almost 600 new minerals, notably those arising from biological (including anthropogenic) processes. Distinctions have been proposed by Perry et al. (2007) between "biominerals" (produced by living cells) and "organominerals" (derived from organic molecules, often

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taphonomic, but not directly produced by cellular activity). We further recognize thousands of biologically-mediated mineral species that form indirectly as a consequence of environmental changes caused by cellular activity - most significantly oxygenic photosynthesis. [#48 - Soil minerals]: Research in paleopedology - the study of ancient soils or "paleosols" - reveals that Earth's terrestrial surface has been coated by fine-grained detrital material for much of its history (Johnson and Watson-Stegner 1987; Holland and Rye 1997; Rye and Holland 1998; Retallack 2001). However, prior to the emergence of land plants at ~ 0.4 Ga soils tended to be thin and mineralogically tied to their host lithologies and subaerial weathering. Soils became much deeper and more complex mineral-producing zones in concert with the development of root systems, most notably following the evolution of symbiotic mycorrhizal fungi (Remy et al. 1994; Paris et al. 1995, 1996; Ueshima and Tazaki 1998). The terrestrial formation of clay minerals in soils, in particular, is estimated to have increased by an order of magnitude with the advent of root systems (Schwartzman and Volk 1989; Barker et al. 1998). We list 71 soil minerals that we attribute to Phanerozoic processes, including more than a dozen Al-rich hydrous minerals from leaching zones in laterites and bauxites (e.g., Helgren and Butzer 1977; Hill et al. 2000). [#49 - Biominerals]: Phanerozoic biomineralization encompasses a fascinating collection of 77 minerals formed by a variety of metabolic processes. Much attention has focused on the biological nano-sculpting of mineral-organic composite materials that play structural roles in organisms. Examples include hydroxylapatite and fluorapatite in directed biomineralization of vertebrates (teeth and bones), inarticulate brachiopod shells,

1252 and stinging nettles; the calcite or aragonite forms of CaCO₃, for example in corals, 1253 mollusks, and foraminifera; and of silica employed by such diverse organisms as diatoms, 1254 sponges, and spinifex grass (Lowenstam and Weiner 1989; Weiner and Wagner 1998; 1255 Dove et al. 2003; Dove 2010; Aparicio and Ginebra 2016; Ensikat et al. 2016; Kattimani 1256 et al. 2016; Endo et al. 2018). Lichtenegger et al. (2002) also reported an unusual 1257 occurrence of atacamite [Cu2(OH)3Cl] in jaws of the bloodworm, Glycera dibranchiate. 1258 Microbially-induced oxidation-reduction reactions have resulted in a variety of mineralization pathways, including reduction of aqueous U⁶⁺ to uraninite (UO₂; Suzuki 1259 1260 and Banfield 1999; Fayek et al. 2005; Hazen et al. 2009; Wufuer et al. 2017); formation 1261 of autunite group uranium phosphates (Liang et al. 2015; Beazley et al. 2017); oxidation 1262 or reduction of iron oxide, sulfide, or sulfates (Pósfai et al. 1998; Akai et al. 1999; Coker 1263 et al. 2008; Boyd and Druschel 2013; Berg et al. 2014, 2020), notably to form internal 1264 "magnetosomes" of magnetite or greigite for microbial navigation (Chang and 1265 Kirschvink 1989; Lins et al. 2007; Pósfai et al. 2013; Uebe and Schüler 2016); and 1266 manganese redox reactions to form a number of species [e.g., vernadite, todorokite, 1267 birnessite, rhodochrosite; Carmichael and Bräuer 2015; Kelm et al. 2015; Li et al. 2016; 1268 Zerfaß et al. 2019; Galezowski et al. 2020; Lu et al. 2021). Some researchers have suggested that seafloor manganese nodules form, at least in part, through such 1269 1270 biochemical processes (Lysyuk 2008; Blöthe et al. 2015). Microbes have also been 1271 invoked in the precipitation of gold (Au; Reith et al. 2006, 2009; Johnston et al. 2013; 1272 Sanval and Shuster 2021), copper carbonate (Li and Gadd 2017), anatase (TiO₂; Ping et 1273 al. 2016), vanadium minerals (Carpentier et al. 2003), and polymorphs of sulfur (Douglas 1274 and Yang 2002; Gleeson et al. 2011; Cron et al. 2019). 1275 Biochemical processes also lead to a variety of incidental minerals (Yoder 2002; 1276 Hazen et al. 2008, their Table 3), as manifest in dozens of human-precipitated minerals, 1277 for example in kidney stones (Rogers 1997; Giannossi et al. 2009) and gallstones (Endo 1278 1962; Dumitraşcu et al. 1984). Finally, the only example of a mineral known to form 1279 exclusively by biomineralization is hazenite [KNaMg₂(PO₄)₂·14H₂O; Yang et al. 2011], 1280 which is excreted by microbes living in the alkali- and P-saturated hypersaline waters of 1281 Mono Lake, California. 1282 [#50 - Coal minerals]: An eclectic assortment of 273 different mineral species has 1283 been identified from coal and/or oil shale minerals, all of which must have been formed 1284 in the past ~300 million years (Saxby 2000; Schweinfurth 2016). As might be expected, several of these phases are crystallized hydrocarbons, such as idrialite (C22H14) and 1285 1286 evenkite (C₂₃H₄₈), or ammonia-bearing minerals, including letovicite [(NH₄)₃H(SO₄)₂] 1287 and godovikovite [(NH₄)Al(SO₄)₂]. Of note is abelsonite (NiC₃₁H₃₂N₄; Milton et al. 1288 1978), the only known geoporphyrin mineral, from the Green River oil shale of Utah. 1289 Coal and oil shale also contain a wide range of fine-grained clay minerals, 1290 oxide/hydroxides, and hydrous sulfates, as well as minerals incorporating relatively rare 1291 metals that are known to concentrate in hydrocarbon-rich deposits, for example 1292 strangersite (SnGeS₃), patronite (VS₄), Laphamite (As₂Se₃), cadmoindite (CdIn₂S₄), 1293 moschelite (HgI), tugarinovite (MoO₂), bismuthinite (Bi₂S₃), and stibnite (Sb₂S₃). Note

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that we also list 234 minerals produced in coal mine fires as a separate anthropogenic paragenetic process [#54]. However, we cannot rule out possible overlaps between those phases and the varied coal minerals listed here [#50]. [#51 – Pyrometamorphic minerals]: Pyrometamorphic minerals of the Hatrurim Formation in the Middle East (Israel and Jordan) include a fascinating suite of 128 species that formed when natural ignition of near-surface hydrocarbon deposits (presumably both natural gas and petroleum) subjected sediments to temperatures in excess of 1000 °C (Gross 1977; Grapes 2006; Sokol et al. 2019). Two-thirds of these minerals are Ca-bearing, some closely resembling phases in cement "clinkers," including such unusual silicates as larnite (Ca₂SiO₄), hatrurite (Ca₃SiO₅), grossite (CaAl₄O₇), and rankinite (Ca₃Si₂O₇). The Hatrurim Formation also hosts unusual Ca sulfides such as oldhamite (CaS) and dzierzanowskite (CaCuS₂), and other phases such as vapnikite (Ca₃UO₆), chromatite (CaCrO₄), and lakargite [Ca(Zr,Sn)O₃]. The Hatrurim Formation is mineralogically unique, but pyrometamorphism has been a persistent phenomenon throughout Earth history, with high-T, low-P alteration occurring in lava xenoliths [#9], during lightning strikes [#29], and as a consequence of anthropogenic coal mine fires [#54] and smelting [#56]. [#52 – Guano/urine minerals]: A curious assortment of 72 mineral species are derived from the urine and guano of birds and bats – minerals preserved primarily in caves and on islands in arid environments. A few of these minerals form directly from excreta, including guanine [C₅H₃(NH₂)N₄O], urea [CO(NH₂)₂], and uricite (C₅H₄N₄O₃). Other minerals result from reactions between urine and prior minerals; spheniscidite

 $[(NH_4)Fe^{3+}_{2}(PO_4)_2(OH)^2H_2O]$ (Wilson and Bain 1986), a fascinating example, is 1316 formed when the urine of penguins (order Sphenisciformes, hence the mineral name) 1317 1318 reacts with layer silicates in soils beneath a rookery on Elephant Island in the British 1319 Antarctic Territory. 1320 [#53 – Taphonomic minerals]: We identify 117 other biologically-derived minerals 1321 with presumed taphonomic origins, mostly formed during the decay and/or fossilization 1322 of wood and other plant material (Behrensmeyer et al. 2000, Mustoe 2018). Plant decay 1323 leads to several distinctive organic minerals (e.g., Garvie 2003), notably oxalates, such as 1324 weddellite $(CaC_2O_4\dot{}_2H_2O)$ and uroxite $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2\dot{}_1H_2O]$, and acetates, including paceite [CaCu(CH₃COO)₄·6H₂O] and hoganite [Cu(CH₃COO)₂·H₂O]. Decay 1325 1326 may also release ammonia, which plays a role in producing 20 taphonomic minerals that 1327 by reaction with NH₄-bearing fluids, for example ammoniozippeite 1328 $[(NH_4)_2(UO_2)_2(SO_4)O_2 \cdot H_2O]$ and ambrinoite $[(K,NH_4)_2(As,Sb)_6(Sb,As)_2S_{13} \cdot H_2O]$. An 1329 intriguing geochemical consequence of wood fossilization is the concentration of 1330 vanadium-rich fluids and formation of at least 14 minerals, including vanoxite (V⁴⁺₄V⁵⁺₂O₁₃·8H₂O) and dreyerite (Bi³⁺V⁵⁺O₄). Burial of organics also commonly 1331 results in subsurface reduction reactions, including U⁶⁺ to U⁴⁺ [e.g., coffinite, 1332 $(U^{4+}SiO_4 \cdot nH_2O)$] and V^{5+} to V^{4+} or V^{3+} [berdesinskiite, $(V^{3+}_2TiO_5)$]. 1333 1334 1335 Stage 10b. Anthropogenic minerals The most recent (and ongoing) stage of mineral 1336 evolution, spanning the past few thousand years but intensifying since the Industrial

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Revolution, encompasses a wide range of more than 600 human-mediated minerals (Catheart 2011; Corcoran et al. 2014; Hazen and Zalaziewski 2019; Zeng et al. 2020). Hazen et al. (2017) reviewed the mineralogy of the so-called "Anthropocene Epoch," tabulating 208 mineral species approved by the IMA-CNMNC that occur principally or exclusively through human activities. The present more inclusive survey of the paragenetic modes of all minerals points to more than 600 mineral species that may form as byproducts of human industry, though most of those phases occur by natural processes, as well. [#54 – Mine fire minerals]: Of more than 500 anthropogenic minerals arising as a consequence of mining activities, we tabulate 234 minerals that form in coal mine fires, both by thermal metamorphism of prior phases and by condensation of new species (Lapham et al. 1980; Grapes 2006; Kruszewski 2013; Stracher et al. 2015). All but 6 of these minerals are also known to form by other processes, mostly by pyrometamorphism [#51] and at volcanic fumaroles ([#11] or [#45]). Those six species unique to coal fires include two intriguing molecular crystals: freitalite (C₁₄H₁₀) is composed of the polycyclic aromatic hydrocarbon, anthracene, which is a major component of coal tar; acetamide (CH₃CONH₂) is the simplest amide (NH₂) compound, which has important uses in the plastics industry. [#55 – Mine-derived minerals]: Mining activities lead to a wealth of new minerals, including those formed by weathering of mine dump phases, formation on mine tunnel walls, precipitation from acid mine drainage systems, and alteration associated with mine timbers and artifacts (Hazen et al. 2017). We recognize 264 of these mining-derived minerals, all but 5 of which also form in natural environments. In particular, 227 of these

1360 species (86 %) also arise through natural near-surface oxidative weathering processes 1361 [#47]. We acknowledge that it is often difficult to discriminate between phases that arose 1362 exclusively because of human mining activities and those that may have formed naturally 1363 through alteration of surface exposures. 1364 [#56 - Slag minerals]: The alteration of minerals through smelting, and in some 1365 instances the subsequent alteration of slag, results in 143 mineral species. This high-1366 temperature processing represents a form of pyrometamorphism (Grapes 2006; Sueoka 1367 and Sakakibara 2013; Kierczak and Ettler 2021), and it produces a similar suite of phases 1368 to other pyrometamorphic mechanisms (e.g., [#9], [#11], [#29], and [#54]). We did not 1369 identify any mineral species that occurs exclusively in slag. 1370 [#57 – Other human-mediated minerals]: Finally, we record an eclectic list of 49 1371 mineral species produced via other human-mediated processes. These phases include 1372 corrosion products of bronze, lead, and other ancient archaeological artifacts, notably Pb-1373 and Cu-bearing phases that have been found associated with the ancient slag deposits at 1374 Laurium, Greece [e.g., atacamite, Cu₂Cl(OH)₃, and laurionite, PbCl(OH); Smith and 1375 Prior 1899]; precipitation of phases in geothermal piping and other mineral-rich 1376 subsurface water systems, such as nasinite [Na₂B₅O₈(OH)·2H₂O] and santite 1377 [KB₅O₆(OH)₄·2H₂O] from Tuscany (Merlino and Sartori 1970); alteration of archived 1378 drill cores or minerals stored in museum drawers, including calclacite 1379 [Ca(CH₃COO)Cl·5H₂O; coalingite Van **Tassel** 1945] and [Mg₁₀Fe³⁺₂(CO₃)(OH)₂₄·2H₂O; Mumpton et al. 1965]; minerals suspected of forming 1380 by grinding [itoite, Pb₃GeO₂(SO₄)₂(OH)₂; Anthony et al. 2003]; fertilizer byproducts 1381

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such as metavariscite [Al(PO₄)·2H₂O; Anthony et al. 2003]; and alteration of discarded lead batteries (e.g., cerussite, PbCO₃). However, none of these phases is unique to anthropogenic activities, in accord with rules of the IMA-CNMNC (e.g., Nickel and Grice 1998). Other minerals that might join this list in the future include alteration phases of discarded lithium batteries, semiconductors and phosphors employed in electronics, and other technological materials (e.g., Galezowski et al. 2020). In addition, purposeful human productions of countless thousands of synthetic phases not considered as minerals by the IMA-CNMNC have dramatically increased the diversity and distribution of mineral-like compounds at or near Earth's surface. Many of these compounds, including building materials, semiconductors, laser crystals, specialty alloys, synthetic gemstones, and possibly even plastic debris, are likely to persist for millions of years in the geologic record, thus providing a clear sedimentary horizon that marks the Anthropocene Epoch (Catheart 2011; Corcoran et al. 2014; Hazen et al. 2017; Hazen and Zalaziewski 2019).

1397 IMPLICATIONS

This study of the paragenetic modes of minerals points to several important trends in mineral evolution, while raising significant unanswered questions. Our preliminary database records 5659 minerals approved by the IMA-CNMNC assigned to 57 paragenetic modes, resulting in 10,556 combinations of a mineral species and a paragenetic mode (Supplementary Table 1). This open-access database is an evolving resource; we welcome additions and corrections.

Several conclusions can be drawn from these data:

• Water is the principal driver of mineral diversity: Of the 5659 minerals examined, 4583 (81.0 %) either incorporate essential OH and/or H₂O, accounting for 3150 of 5659 mineral species (55.7 %), or they are anhydrous phases that were formed through the action of aqueous fluids, for example, by dehydration, evaporation, or precipitation from a hydrothermal solution (1433 species). No other physical or chemical factor comes close to this dominant role of water in creating mineral diversity. Near-surface hydration and weathering represent obvious major factors in this variety, resulting in more than 2000 species. We suggest that subduction and the deep-water cycle is comparable in its influence on Earth's mineralogy as a consequence of the selection and concentration of rare elements through water-rock interactions in large volumes of the upper mantle and crust. The sharp contrast between Earth's large complement of minerals and the relative mineralogical parsimony of the Moon and Mercury, as well as the modest diversity found on Mars, stems from differing influences of water.

Biology plays an important role in Earth's mineral diversity (but not quite as much as previously suggested): We find that almost half of Earth's minerals – 2707 of 5659 species (47.8 %) – are known to form as a result of biological influences. More than 2000 of these minerals occur as a consequence of near-surface oxidative weathering/alteration of prior phases, which is the second most important factor in Earth's mineral diversity after water. Many minerals also form as coal-related and other taphonomic minerals (597 species), as well as anthropogenic minerals, for example as byproducts of mining (603 minerals). However, contrary to previous estimates, we find that only ~34% of mineral species form exclusively as a consequence of biological processes, in contrast to the estimate of two-thirds by Hazen et al. (2008). Nevertheless, the appearance of more than 1900 minerals exclusively through biology represents a significant, pervasive planetary biomarker (Chan et al 2019; Johnson et al. 2020).

Rare elements are important in Earth's mineral diversity: As noted above, 41 rare mineral-forming elements present in Earth's crust at less than 5 ppm are essential constituents in ~2400 mineral species. These scarce elements, including chalcogenides (As, Sb, Se, Te), transition metals (Cd, Mo, Sn), platinum group elements, and rare earth elements, represent fewer than 1 in 10,000 crustal atoms, yet they are essential in 42.4 % of minerals (https://rruff.info/ima, accessed 7 March 2021) – far more species than might be expected based on crustal abundances. We suggest that interactions between host rocks with trace amounts of these elements and aqueous fluids, especially with varied anionic species that select and concentrate metal ions, are the principal factor in creating local chemical anomalies with extreme

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rare element concentrations. This observation is consistent with the occurrence of mineral-rich localities associated with complex granite pegmatites, agpaitic rocks, and many hydrothermal ore deposits. In the context of evolving complex systems, including natural ecosystems and human societies, it is significant that the presence of a few exotic individuals has the potential to greatly enhance system diversity.

Most minerals are known to form by only one paragenetic process: Most mineral species – 3349 of 5659, or 59.2 % – are known to form by only one of our proposed 57 paragenetic modes. An additional 1372 species (24.2 %) have two known paragenetic modes, whereas 458 species (8.1 %) have three. By contrast, only 26 minerals, all of them familiar and abundant rock-forming phases (Deer et al. 1982-2013), are known to form in 12 or more different ways. Pyrite boasts the most diverse range, with 21 paragenetic modes, including igneous, metamorphic, sedimentary, and alteration host lithologies; encompassing both abiotic and biotic processes; and spanning more than 4.5 billion years of Earth history, from preterrestrial asteroid alteration (> 4.56 Ga) to precipitation in anthropogenic mine environments (< 1 Ka). Other widely-forming species with 14 or more paragenetic modes include albite, corundum, hematite, and magnetite (with 18 modes); calcite, hornblende, and rutile (17); baryte (15); and forsterite, ilmenite, quartz, and sphalerite (14). Note that the previous finding that most minerals are rare, found at five or fewer localities (Hazen et al. 2015; Hystad et al. 2015; Hazen and Ausubel 2016), mirrors the observation that most minerals have only one mode of formation.

Our work also raises intriguing questions that will drive future investigations:

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Does Earth's mineralogy display a progressive rise in complexity? Pioneering work on the quantification of mineral complexity by Sergey Krivovichev (2012, 2013, 2014, 2015, 2016) facilitates testing of hypotheses related to increased mineral complexity through time. Preliminary work has been applied to suites of minerals based on composition (Grew et al. 2016, 2017; Morrison et al. 2020) or approximate stage in Earth history (Krivovichev et al. 2018). The present study offers the opportunity to probe the evolving complexity of Earth's minerals in greater depth, by considering the relative influences of temperature, pressure, and/or composition in various mineral-forming environments as a function of geological time. Quantitative investigations of whether, and if so how, mineral system complexify over time could provide a rigorous test of models of cosmic chemical evolution (e.g., Zaikowski and Friedrich 2007). What mineral-forming environments occur on the Moon, Mars, and other terrestrial worlds? Enumerating paragenetic modes, and placing each mineral species into one or more of those categories, offers an opportunity to evaluate extraterrestrial mineralogy with a new perspective. If Mars had (or still has) a hydrological cycle, what mineralogical manifestations might we expect? For example, are there Martian hydrothermal sulfide deposits and, if so, were a variety of metals mobilized? On the other hand, if the Moon is truly dry, then what paragenetic processes are excluded? And do extraterrestrial bodies display paragenetic processes not seen on Earth, such

• What role did minerals play in the origins of life? A recurrent theme in recent studies of Earth's evolving crust, in particular the tectonic processes that shaped it, is

as cryo-volcanism on Titan (Maynard-Casely et al. 2018; Hazen 2018).

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speculation that many of Earth's mineral-forming processes may have occurred much earlier than previously modeled. The formation of oceans prior to 4.45 Ga, the extensive development of continental crust by 4.4 Ga, and perhaps even the initiation of some form of subduction-driven plate tectonics in the early Hadean Eon, push many important mineral-forming processes to Earth's first 250 million years. These scenarios, if true, have important implications for models of mineral evolution and the origins of life. Previous estimates of Hadean mineral diversity posited mineralogical parsimony, with only a few hundred species prior to 4 Ga (Hazen 2013; Morrison et al. 2018). However, this new tabulation of mineral paragenetic modes, coupled with recent estimates of the rapid evolution of a dynamic early Hadean Earth, suggest that as many as 3534 mineral species – the collective inventories of modes [#1] through [#43] – may have formed within Earth's first 250 million years. If so, then most of the geochemical and mineralogical environments invoked in models of life's origins would have been present by 4.3 Ga. If life is rare in the universe, requiring an idiosyncratic sequence of unlikely chemical reactions (Hazen 2017), then this view of a mineralogically diverse early Earth provides many more plausible reactive pathways over a longer timespan than previous models. If, on the other hand, life is a cosmic imperative that emerges on any mineral- and water-rich world, then these findings support the hypothesis that life on Earth emerged rapidly, in concert with a vibrant, diverse Mineral Kingdom, in the earliest stages of planetary evolution.

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This work would not have been possible without the remarkable publication of multivolume references, especially Rock-Forming Minerals (Deer et al. 1982-2013) and The Handbook of Mineralogy (Anthony et al. 1990-2003), as well as ongoing efforts to develop and expand comprehensive open-access data resources, especially by Jolyon Ralph, founder of mindat.org, and Robert T. Downs, founder of rruff.info. Collectively, these mineral informatics pioneers are empowering a new age of data-driven discovery in mineralogy. We are deeply grateful to Raquel Alonso Perez, Daniel Hummer, Sergey Krivovichev, Michael Walter, and Nathan Yee, who provided detailed, thoughtful, and constructive reviews that significantly improved an early version of this contribution. George Harlow and Andrea Kozoil contributed comprehensive reviews of the penultimate manuscript. We are also grateful to Robert Downs, Paul Falkowski, Frank Hawthorne, Peter Heaney, Jun Korenaga, Jeffrey Post, Simone Runyon, and Steven Shirey for thoughtful discussions and comments. This publication is a contribution to the 4D Initiative and the Deep-time Digital Earth (DDE) program. Studies of mineral evolution and mineral ecology have been supported by the Alfred P. Sloan Foundation, the W. M. Keck Foundation, the John Templeton Foundation, NASA Astrobiology Institute (Cycle 8) ENIGMA: Evolution of Nanomachines In Geospheres and 329 Microbial Ancestors (80NSSC18M0093), a private foundation, and the Carnegie Institution for Science. Any opinions, findings, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the National Aeronautics and Space Administration.

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Table 1. Chronological list of 57 paragenetic modes of minerals, with numbers of associated mineral species

Paragenetic Mode*	Age (Ga)	#Species**	#Unique***	Ref.****
Pre-terrestrial "Ur-minerals"	> 4.57	30	8	
Stellar atmosphere condensates		$\frac{30}{22}$	<u>8</u> 1	1-4
2. Interstellar condensates****		8	7	5-7
Stage 1: Primary nebular phases	<u>4.567—4.561</u>	<u>86</u>	<u>14</u>	
3. Solar nebular condensates (CAIs, AOAs, URIs)	> 4.565	48	<u>14</u> 14	7-12
4. Primary chondrule phases	4.566—4.561	47	0	11-15
Stage 2: Planetesimal differentiation & alteration	4.566—4.550	<u> 261</u>	<u>65</u> 21	
5. Primary asteroid phases	4.566—4.560	94	21	11,13,16-18
6. Secondary asteroid phases	4.565—4.550	205	44	11,12,16,17,19-21
Stage 3a: Earth's earliest Hadean crust	<i>> 4.50</i>	<u>400</u>	<u>61</u>	22-26
7. Ultramafic igneous rocks		123	10	22,23,27
8. Mafic igneous rocks		93	6	22,23,28-33
9. Lava/xenolith minerals (hornfels, sanidinite facies)		127	8	22,23,34
10. Basalt-hosted zeolite minerals			30	35
11. Volcanic fumarole minerals; reduced phases (see also [#45])		36	7	34,36
Stage 3b: Earth's earliest hydrosphere	<i>> 4.45</i>	<u>350</u>	<u>64</u>	37,38
12. Hadean hydrothermal subsurface sulfide deposits (see also [#33])			48	39-43
13. Hadean serpentinization			8	44-49
14. Hot springs, geysers, and other subaerial geothermal minerals			1	35,50
15. Black/white smoker minerals and other seafloor hydrothermal minerals			0	46,51,52
16. Low-T aqueous alteration of Hadean subaerial lithologies (see also [#23])			3	35,50
17. Marine authigenic Hadean minerals (see also [#24])			1	35
18. Minerals formed by freezing			3	53

Stage 4a: Earth's earliest continental crust	> 4.4—3.0	<u>2385</u>	<u>1031</u>	22,23,54-57
Igneous rocks		<u>160</u>	<u>17</u>	
19. Granitic intrusive rocks		143	15	22,23,58
20. Acidic volcanic rocks		45	2	22,23,59
Near-surface Processes		<u>1113</u>	<u>244</u>	
21. Chemically precipitated carbonate, phosphate, iron for	mations	79	3	28,60-67
22. Hydration and low-T subsurface aqueous alteration (se	e also [#23])	247	85	37,38,68-70
23. Subaerial aqueous alteration by non-redox-sensitive flu	iids (see also [#47]) 398	79	71
24. Authigenic minerals in terrestrial sediments (see also [#1 <i>7</i>])	74	0	35,71,72
25. Evaporites (prebiotic)		210	65	57,62,73
26. Hadean detrital minerals		250	7	74
27. Radioactive decay; auto-oxidation		9	0	75-77
28. Photo-alteration, pre-biotic		10	0	78
29. Lightning-generated minerals		7	0	34,79-81
30. Terrestrial impact minerals		16	5	82,83
High-T alteration and/or metamorphism		<u>1505</u>	<u>770</u>	
31. Thermally altered carbonate, phosphate, and iron form	ations	356	89	28,60-66
32. Ba/Mn/Pb/Zn deposits, including metamorphic deposit	S	412	185	40,68,84
33. Minerals deposited by hydrothermal metal-rich fluids ((see also [#12])	797	496	37-43
Stage 4b: Highly evolved igneous rocks	> 3.0	<u>1476</u>	<u>662</u>	
34. Complex granite pegmatites		564	238	85-88
35. Ultra-alkali and agpaitic igneous rocks		726	377	89,90
36. Carbonatites, kimberlites, and related igneous rocks		291	40	40,91-97
37. Layered igneous intrusions and related PGE minerals		135	7	40,98-100
Stage 5: Initiation of plate tectonics	< 3.5—2.5	<u>458</u>	<u>56</u>	101-107
38. Ophiolites		108	7	108-111
39. High-P metamorphism (blueschist, eclogite, ultrahigh l	P facies)	70	12	112-118

DOI: https://doi.org/10.2136/am-2022-608	19. Http://www.H	iinsocam.org/		
40. Regional metamorphism (greenschist, amphibolite, granulite	facies)	319	36	117,118
41. Mantle metasomatism		16	1	119,120
42. Sea-floor Mn nodules		15	0	121-123
43. Shear-induced minerals (including mylonite/slickensides)		9	0	124,125
Stage 6: Anoxic biosphere	< <i>4.0</i>			
44. Anoxic microbially-mediated minerals (see also [#44])		11	0	126-141
Stage 7: Great Oxidation Event	< 2.4	<u>2328</u>	<u>1298</u>	142-147
45. Oxidized fumarolic minerals (see also [#11])		<u>424</u>	<u>168</u>	34,36
a. [Sulfates, arsenates, selenates, antimonates]		[253]	[116]	
b. [Other oxidized fumarolic minerals]		[276]	[108]	
46. Near-surface hydrothermal alteration of minerals (see also [#.	22])	52	11	37,38,148
47. Low-T subaerial oxidative hydration, weathering (see also [#.		1998	<u>1119</u>	148
a. [Near-surface hydration of prior minerals]	J L J.	[1649]	[956]	
b. [Sulfates and sulfites]		[409]	[185]	
c. [Carbonates, phosphates, borates, nitrates]		[577]	[338]	
d. [Arsenates, antimonates, selenates, bismuthinates]		[505]	[361]	
		[372]	[229]	
 e. [Vanadates, chromates, manganates] f. [Uranyl (U⁶⁺) minerals] 		[236]	[173]	149,150
g. [Halogen-bearing surface weathering minerals]		[236]	[121]	1.5,120
h. [Near-surface oxidized, dehydrated minerals]		[316]	[176]	
i. [Terrestrial weathering of meteorites]		[28]	[10]	11
i. [Terrestrial weathering of ineteorites]		[20]	[10]	11
Stage 8: "Intermediate Ocean" (no new paragenetic modes)	1.9—0.9	0	0	151-155
stage of Thermediate occur (no her paragenetic modes)	1.5 0.5	Ü	v	101 100
Stage 9: "Snowball Earth" (no new paragenetic modes)	0.9—0.6	0	0	156-158
Single 5. Sino nount 2 min (no non pun agonemo mones)	0.5	Ü	v	100 100
Stage 10a: Neoproterozoic oxygenation/terrestrial biosphere	< 0.6	<u>597</u>	<u>72</u>	
48. Soil leaching zone minerals	< 0.6	71	4	159-166
49. Oxic cellular biomineralization (see also [#44])	< 0.54	77	1	136,167-186
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50. Coal and/or oil shale minerals	< 0.36	273	4	187,188
51. Pyrometamorphic minerals (see also [#54] & [#56])	< 0.36	128	32	34,189,190
52. Guano- and urine-derived minerals	< 0.4	72	17	191,192
53. Other minerals with taphonomic origins	< 0.4	117	14	193,194
Stage 10b: Anthropogenic minerals	< 10 Ka	<u>603</u>	<u>11</u>	195-199
54. Coal and other mine fire minerals (see also [#51] & [#56])		234	6	34,200-202
55. Anthropogenic mine minerals		264	5	197
56. Slag and smelter minerals (see also [#51] & [#55])		143	0	34,197,203-204
57. Other minerals formed by human processes		49	0	195-199, 205,206

^{*} The 10 stages of mineral evolution refer to temporal divisions, as outlined in Table 1 of Hazen et al. (2008). The 57 paragenetic modes are designated by [#1] to [#57].

Numbered references: 1 = Hazen & Morrison (2020); 2 = Zinner (2014); 3 = Nittler & Ciesla (2016); 4 = Boujibar et al. (2021); 5 = Whittet (2003); 6 = Gibb et al. (2004); 7 = Morrison & Hazen (2020); 8 = MacPherson (2014); 9 = Krot et al. (2004); 10 = El Goresy et al. (2002); 11 = Rubin & Ma (2021); 12 = Brearley & Jones (1998); 13 = Krot et al. (2014); 14 = Russell et al. (2018); 15 = Hazen et al. (2021); 16 = Mittlefehldt et al. 1998; 17 = Mittlefehldt (2014); 18 = Morrison & Hazen (2021); 19 = McSween et al. (1988); 20 = Hazen & Morrison (2021); 21 = Tomioka & Miyahara (2017); 22 = Rollinson (2007b); 23 = Van Kranendonk et al. (2007b); 24 = Papineau (2010); 25 = Hazen (2013); 26 = Morrison et al. (2018); 27 = Korenaga (2021); 28 = Isley & Abbott (1999); 29 = O'Neil et al. (2008); 30 = Ashwal (1993); 31 = Prokoph et al. (2004); 32 = O'Neil et al. (2008); 33 = Ernst (2014); 34 = Grapes (2006); 35 = Deer et al. (2004); 36 = Vergasova & Filatov (2016); 37 = Heinrich and Henley (1989); 38 = Pirajno (2009); 39 = Laznicka 1973; 40 = Meyer (1988); 41 = Groves et al. (2005); 42 = Huston et al. (2010); 43 = Jenkin et al. (2015); 44 = Blais & Auvray (1990); 45 = Lowell & Rona (2002); 46 = Palandri & Reed (2004); 47 = Shrenk et al. (2013); 48 = Holm et al. (2015);

^{**} Numbers of species are based on paragenetic modes identified for 5659 IMA-approved mineral species, as tabulated on https://rruff.info/ima (accessed 23 November 2020).

^{***} Numbers of species known to form only by that paragenetic mode.

^{****} **References:** General references for mineral paragenetic modes include Anthony et al. (1990-2003); Deer et al. (1982-2013); and https://rruff.info/ima and https://mindat.org, and references therein (accessed 17 March 2021).

49 = Menez et al. (2018); 50 = Wilson (2013); 51 = Hekinian et al. (1980); 52 = Haymon and Kastner (1981); 53 = Genceli Güner et al. (2013); 54 = Wilde et al. (2001); 55 = Kemp & Hawkesworth (2003); 56 = Kemp et al. (2007); 57 = Johnson et al. (2017); 58 = Chappell & White (2001); 59 = Sugitani et al. (2003); 60 = Falkowski et al. 2000; 61 = Klein (2005); 62 = Button (1982); 63 = Anbar & Holland (1992); 64 = Bekker et al. (2010); 65 = Barturin & Bezrukov (1979); 66 = Delaney (1998); 67 = Crevello et al. (1989); 68 = Post (1999); 69 = Savage et al. (1987); 70 = Nishimoto & Yoshido (2010); 71 = Chang et al. (1996); 72 = Holland & Rye (1997); 73 = Buick & Dunlop (1990); 74 = Baker (1962); 75 = Frondel (1958); 76 = Finch & Murakami (1999); 77 = Hazen et al. (2009); 78 = Kim et al. (2013); 79 = Essene & Fisher (1986); 80 = Pasek et al. (2012); 81 = Hess et al. (2021); 82 = Tomioka & Miyahara (2017); 83 = Tschauner (2019); 84 = Leach et al. (2010); 85 = London (2008); 86 = Tkachev (2011); 87 = Grew et al. (2017); 88 = Grew et al. (2019); 89 = Marks & Markl (2017); 90 = Mikhailova et al. (2019); 91 = Patchett et al. (1982); 92 = Bell (1989); 93 = Downes et al. (2012); 94 = Jones et al. (2013); 95 = Mitchell et al. (2019); 96 = Woolley & Kjarsgaard (2008); 97 = Heaman et al. (2019); 98 = Naldrett et al. (1987); 99 = Maier & Groves (2011); 100 = Zientek (2012); 101 = Stern (2005); 102 = Rollinson (2007a); 103 = Condie & Pease (2008); 104 = Shirey et al. (2008); 105 = Shirey and Richardson (2011); 106 = Bauer et al. (2020); 107 = Reimink et al. (2019); 108 = Bai et al. (2011); 109 = Moores (2002); 110 = Dilek (2003); 111 = Furnes et al. (2007); 112 = Chopin (1984); 113 = Hacker (2006); 114 = Palin and White (2016); 115 = Zheng and Chen (2017); 116 = Brown (2007); 117 = Philpotts & Ague (2009); 118 = Vernon (2008); 119 = Luth (2003); 120 = O'Reilly and Griffin (2012); 121 = Hlawatsch et al. (2002); 122 = Fike et al. (2006); 123 = Wegorzewski & Kuhn (2014); 124 = Passchier & Trouw (2005); 125 = Trouw et al. (2009); 126 = Van Kranendonk et al. (2003); 127 = Akai et al. (1999); 128 = Allwood et al. (2006); 129 = Anbar & Holland (1992); 130 = Banerjee (1971); 131 = Frankel & Bazylinski (2003); 132 = Grotzinger & Knoll (1999); 133 = Konhauser et al. (2005); 134 = Kappler et al. (2005); 135 = Schulz & Schulz (2005); 136 = Southam & Saunders (2005); 137 = Lepot et al. (2008); 138 = Marshall (1979); 139 = Burnett & Riggs (1990); 140 = Chauhan (1979); 141 = Cook & Shergold (1990); 142 = Sverjensky & Lee (2010); 143 = Hazen (2015); 144 = Jabłońska & Tawfik (2021); 145 = Canfield (2014); 146 = Lyons et al. (2014); 147 = Anbar et al. (2007); 148 = Anthony et al. (1990-2003); 149 = Nash et al. (1981); 150 = Hazen et al. (2009); 151 = Brasier (1998); 152 = Buick et al. (1995); 153 = Anbar & Knoll (2002); 154 = Brasier (2012); 155 = Mukherjee et al. (2018); 156 = Kirschvink (1992); 157 = Hoffman et al. (1998); 158 = Bodiselitsch et al. (2005); 159 = Johnson and Watson-Stegner (1987); 160 = Holland and Rye (1997); 161 = Rye and Holland (1998); 162 = Retallack (2001); 163 = Kennedy et al. (2006); 164 = Ueshima & Tazaki (1998); 165 = Helgren and Butzer (1977); 166 = Hill et al. (2000); 167 = Yoder (2002); 168 = Dove et al. (2003); 169 = Dove (2010); 170 = Lowenstam & Weiner 1989; 171 = Ensikat et al. (2016); 172 = Endo et al. (2018); 173 = Lichtenegger et al.

(2002); 174 = Zuzuki & Banfield (1999); 175 = Wufuer et al. (2017); 176 = Beazley et al. (2017); 177 = Berg et al. (2020); 178 = Pósfai et al. (2013); 179 = Uebe and Schüler (2016); 180 = Kelm et al. (2015); 181 = Reith et al. (2009); 182 = Li & Gadd (2017); 183 = Cron et al. (2019); 184 = Carmichael & Bräuer (2015); 185 = Weiner & Wagner (1998); 186 = Kattimani et al. (2016); 187 = Saxby (2000); 188 = Schweinfurth (2016); 189 = Gross (1977); 190 = Sokol et al. (2008); 191 = Audra et al. (2017); 192 = Audra et al. (2018); 193 = Behrensmeyer et al. (2000); 194 = Mustoe (2018); 195 = Catheart (2011); 196 = Corcoran et al. (2014); 197 = Hazen et al. (2017); 198 = Hazen & Zalaziewski (2019); 199 = Zeng et al. (2020); 200 = Lapham et al. (1980); 201 = Kruszewski (2013); 202 = Stracher et al. (2015); 203 = Sueoka & Sakakibara (2013); 204 = Kierczak & Ettler (2021); 205 = Merlino & Sartori (1970); 206 = Smith & Prior (1899)

***** Includes 7 interstellar ice phases that are not IMA-approved mineral species.