



Chapter 1

Mineral Evolution: Episodic Metallogensis, the Supercontinent Cycle, and the Coevolving Geosphere and Biosphere

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Abstract

Analyses of temporal and geographic distributions of the minerals of beryllium, boron, copper, mercury, and molybdenum reveal episodic deposition and diversification. We observe statistically significant increases in the number of reported mineral localities and/or the appearance of new mineral species at ~2800 to 2500, ~1900 to 1700, ~1200 to 1000, ~600 to 500, and ~430 to 250 Ma. These intervals roughly correlate with presumed episodes of supercontinent assembly and associated collisional orogenies of Kenorland (which included Superia), Nuna (a part of Columbia), Rodinia, Pannotia (which included Gondwana), and Pangea, respectively. In contrast, fewer deposits or new mineral species containing these elements have been reported from the intervals at ~2500 to 1900, ~1700 to 1200, 1000 to 600, and 500 to 430 Ma. Metallogensis is thus relatively sparse during periods of presumed supercontinent stability, breakup, and maximum dispersion.

Variations in the details of these trends, such as comparatively limited Hg metallogensis during the assumed period of Rodinia assembly; Proterozoic Be and B mineralization associated with extensional environments; Proterozoic Cu, Zn, and U deposits at ~1600 and 830 Ma; and Cenozoic peaks in B, Cu, and Hg mineral diversity, reveal complexities in the relationship between episodes of mineral deposition and diversification on the one hand, and supercontinent assembly and preservational biases on the other. Temporal patterns of metallogensis also reflect changing near-surface environments, including differing degrees of production and preservation of continental crust; the shallowing geotherm; changing ocean chemistry; and biological influences, especially those associated with atmospheric oxygenation, biomineralization, and the rise of the terrestrial biosphere. A significant unresolved question is the extent to which these peaks in metallogensis reflect true episodicity, as opposed to preservational bias.

Introduction

Earth's near-surface mineralogy has diversified over more than 4.5 b.y. from no more than a dozen preplanetary refractory mineral species (what have been referred to as “ur-minerals” by Hazen et al., 2008) to ~5,000 species (based on the list of minerals approved by the International Mineralogical Association; <http://rruff.info/ima>). This dramatic diversification is a consequence of three principal physical, chemical, and biological processes: (1) element selection and concentration (primarily through planetary differentiation and fluid-rock interactions); (2) an expanded range of mineral-forming environments (including temperature, pressure, redox, and activities of volatile species); and (3) the influence of the biosphere. Earth's history can be divided into three eras and ten stages of “mineral evolution” (Table 1; Hazen et al., 2008), each of which has seen significant changes in the planet's near-surface mineralogy, including increases in the number of mineral species; shifts in the distribution of those species; systematic changes in major, minor, and trace element and

isotopic compositions of minerals; and the appearance of new mineral grain sizes, textures, and/or morphologies.

Initial treatments of mineral evolution, first in Russia (e.g., Zhabin, 1979; Yushkin, 1982) and subsequently in greater detail by our group (Hazen et al., 2008, 2009, 2011, 2013a, b; Hazen and Ferry, 2010; Hazen, 2013), focused on key events in Earth history. The 10 stages we suggested are Earth's accretion and differentiation (stages 1, 2, and 3), petrologic innovations (e.g., the stage 4 initiation of granite magmatism), modes of tectonism (stage 5 and the commencement of plate tectonics), biological transitions (origins of life, oxygenic photosynthesis, and the terrestrial biosphere in stages 6, 7, and 10, respectively), and associated environmental changes in oceans and atmosphere (stage 8 “intermediate ocean” and stage 9 “snowball/hothouse Earth” episodes). These 10 stages of mineral evolution provide a useful conceptual framework for considering Earth's changing mineralogy through time, and episodes of metallization are often associated with specific stages of mineral evolution (Table 1). For example, the formation of complex pegmatites with Be, Li, Cs, and Sn mineralization could not have occurred prior to stage 4 granitization. Similarly, the appearance of large-scale volcanogenic

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TABLE 1. Three Eras and Ten Stages of Mineral Evolution of Terrestrial Planets, with Possible Timing on Earth, Examples of Minerals, and Estimates of the Cumulative Number of Different Mineral Species¹

Stage	Age (Ma) ²	Examples of minerals	~ Cumulative no. of species
Era I: Planetary accretion	>4550		
Primary chondrite minerals	>4560	Mg olivine/pyroxene, Fe-Ni metal, FeS, CAIs	60
Planetesimal alteration/differentiation	>4560–4550		250
Aqueous alteration		Phyllosilicates, hydroxides, sulfates, carbonates, halite	
Thermal alteration		Albite, feldspathoids, biopyriboles	
Shock phases		Ringwoodite, majorite, akimotoite, wadsleyite	
Achondrites		Quartz, K-feldspar, titanite, zircon	
Iron meteorites		Many transition metal sulfides and phosphates	
Era II: Crust and mantle reworking	<4550 Ma-present		
Igneous rock evolution	4550–4000		350 to 500 ³
Fractionation		Feldspathoids, biopyriboles	
Volcanism, outgassing, surface hydration		Hydroxides, clay minerals	
Granite formation	Uncertain; <4400		1,000
Granitoids		Quartz, alkali feldspar (perthite), hornblende, micas, zircon	
Pegmatites		Beryl, tourmaline, spodumene, pollucite, many others	
Plate tectonics	Uncertain; >3000		1,500
Hydrothermal ores		Sulfides, selenides, arsenides, antimonides, tellurides, sulfosalts	
Metamorphic minerals		Kyanite, sillimanite, cordierite, chloritoid, jadeite, staurolite	
Anoxic biological world	>3900–2500		1,500
Metal precipitates		Banded iron formations (Fe and Mn)	
Carbonates		Ferroan carbonates, dolostones, limestones	
Sulfates		Barite, gypsum	
Evaporites		Halides, borates	
Carbonate skarns		Diopside, tremolite, grossularite, wollastonite, scapolite	
Era III: Biomediated mineralogy	>2500-present		
Paleoproterozoic atmospheric changes	<2500		>4500
Surface oxidation	>2000	New oxide/hydroxide species, especially ore minerals	
Intermediate ocean	1850–850	Minimal mineralogical innovation	>4500
Neoproterozoic biogeochemical changes	850–542		>4500
Glaciation		Extensive ice deposition, but few new minerals	
Postglacial oxidation		Extensive oxidative weathering of all surface rocks	
Phanerozoic Era	542-present		>4800
Biomineralization		Extensive skeletal biomineralization of calcite, aragonite, dolomite, hydroxyapatite, and opal	
Bioweathering		Increased formation of clay minerals, soils	

¹Note that the timings of some of these stages are poorly resolved, some stages overlap, and several stages continue to the present (revised after Hazen et al., 2008)

²The timings and durations, and thus in some cases the sequence, of several stages are matters of debate; for example, it is uncertain whether subduction-driven plate tectonics, extensive granitization, and the formation of complex pegmatites pre- or postdated the origins of life (Hazen, 2013, and references therein); Cawood and Hawkesworth (2014) propose 1700–750 Ma as the stage 8 intermediate ocean based on tectonic and geochemical evidence

³Three hundred and fifty species on a volatile-poor planet (Mercury; Moon); 500 species on a volatile-rich planet (Mars)

sulfide deposits may postdate the initiation of modern-style subduction (stage 5). The origins and evolution of life also played central roles; for example, redox-mediated ore deposits of elements such as U, Mo, and Cu occurred only after the Great Oxidation Event (stage 7), and major Hg deposition is associated with the rise of the terrestrial biosphere (stage 10; Hazen et al., 2012).

However, whereas the first appearances of these and other ore deposits most likely occurred subsequent to the beginning of the relevant stages, most ore-forming mechanisms were repeated episodically over billions of years and thus do not closely follow the 10-stage mineral evolution chronology. Inventories of the temporal distributions of major ore deposits (Gastil, 1960; Laznicka, 1973; Meyer, 1981, 1985, 1988; Rundqvist, 1982; Domarev, 1984; Barley and Groves, 1992; Stowe, 1994; Goldfarb et al., 2001; Groves et al., 2005, 2010; Kerrich et al., 2005; Condie et al., 2009, 2011; Condie and

Aster, 2010; Huston et al., 2010; Tkachev, 2011; Cawood and Hawkesworth, 2013; Nance et al., 2014), as well as detailed studies of minerals of the elements Be, B, Hg, and Mo (Grew and Hazen, 2010a, b, 2013, 2014; Grew et al., 2011; Hazen et al., 2012; Golden et al., 2013) have revealed an episodicity in mineralization that is not closely correlated with these 10 stages of mineral evolution. Rather, these and other metallic elements display temporal distributions that, to a first approximation, correlate with intervals of presumed supercontinent assembly and associated production and preservation of continental crust. Additional nuances in metallogeny through the past 3.8 b.y. relate to differences in the character of tectonic processes, changing near-surface environments, and influences of the evolving biosphere and thus add richness to the mineral evolution story. In this review we examine these recent data in the context of more than half a century of similar studies, speculate on their significance, and pose a

set of unanswered questions that may frame future mineral evolution studies.

Episodic Mineralization

Metal ore formation requires both a geochemical mechanism to select and concentrate the metal element, and at least one stable mineral phase that can incorporate that element. In some cases a rare metal element is crystal chemically so similar to a common rock-forming element, as is the case with gallium (Ga^{3+}) substitution for aluminum in octahedral coordination, that natural concentration mechanisms are limited. Thus, gallium is mined principally as a byproduct of bauxite aluminum ore, and only five mineral species are known with essential gallium. By contrast, a number of rare elements, including B, Be, Hg, Mo, and many other metals, are incompatible, i.e., crystal chemically distinct and thus not easily incorporated by solid solution into any minerals of the 12 major elements (Si, Mg, Fe, Al, Ca, Na, K, Mn, Ti, O, S, and H). Consequently, these rare elements form numerous other minerals, including major ore minerals.

Skinner (1976) used such crystal chemical and abundance characteristics to distinguish between the major metal elements, such as Fe, Mn, Al, and Ti, and dozens of less abundant metals, such as Au, Hg, Pb, Zn, and the rare earth elements. An important consequence of this dichotomy is that ores of the major metals are essentially inexhaustible, with the highest grade surface deposits of oxides and sulfides mined first, followed by increasingly larger volumes of progressively lower grade ores. Rare metals, on the other hand, are easily extracted only from concentrated mineralized zones. Skinner (1976) postulated that once those relatively rare high-grade deposits are exhausted, remaining reserves will be in the form of trace element solid solution in other minerals. Thus, once the readily mined near-surface deposits are exhausted, it may become economically unviable to recover those metals. These crystal chemical and abundance factors provide an important context for any consideration of episodic metallogenesis.

Episodicity in mineralogy and petrology

The phenomenon of episodic igneous activity and associated mineralization (Runcorn, 1962; Zhabin, 1979; Meyer, 1981, 1985, 1988; Barley and Groves, 1992) has been placed on a quantitative basis by several authors who have noted striking correlations between the supercontinent cycle and varied modes of mineralization (e.g., Huston et al., 2010; Bradley, 2011; Kaur and Chaudhri, 2014; Nance et al., 2014). Episodicity in mineralization for a wide variety of lithologies, including diverse ultramafic to acidic igneous deposits, marine and continental sedimentary formations, and numerous types of ore deposits, have been reported in more than three decades of compilations (Meyer, 1981, 1985, 1988; Klein, 2005; Goldfarb et al., 2010; Bradley, 2011; Tkachev, 2011). More recently, a number of investigations focus on the temporal distribution of specific minerals, notably zircon (ZrSiO_4) because of the potential of obtaining reliable ages using U-Pb isotopes (Campbell and Allen, 2008; Rino et al., 2008; Condie et al., 2009, 2011; Condie and Aster, 2010; Hawkworth et al., 2010; Voice et al., 2011), but also molybdenite (MoS_2 ; Golden et al., 2013), and the minerals of specific

elements, including beryllium (Grew and Hazen, 2013, 2014), boron (Grew and Hazen, 2010a, b; Grew et al., 2011), lithium (Bradley and McCauley, 2013), and mercury (Hazen et al., 2012). This research has focused on determining the temporal distribution of localities for these minerals, as well as their first appearance (and also intermediate and most recent occurrences in the study of Be minerals by Grew and Hazen, 2014) in the geologic record. These efforts are being conducted in parallel with the development of a “mineral evolution database,” which records ages and mineral species for numerous mineral-bearing deposits (Hazen et al., 2011).

Histograms of frequency versus age for these varied minerals reveal similarities, as well as important differences. Here we introduce and contrast six such histograms (Fig. 1), with the objective of establishing a basis for comparison with future compilations. Note that because of the minimal numbers of data in our preliminary surveys of Be, B, Cu, Mo, and Hg, we are not yet able to apply extensive statistical analysis, such as Monte Carlo kernel density estimation (Aster et al., 2004; Condie and Aster, 2010). We therefore employ a relatively large bin width of 50 Ma in all our analyses.

Determination of mineral ages

Establishing the age of a specific mineral species in a mineral deposit is not always straightforward. In the case of zircon (Fig. 1A) and molybdenite (Fig. 1E) ages are usually determined from radiometric dating (U-Pb and Re-Os methods, respectively) of individual grains. However, high-resolution studies of zoned crystals may reveal significant age gradients from the core to rims of some grains. For example, Aleinkoff et al. (2012) reported multiple age components (941–954 Ma) for individual molybdenite grains from Proterozoic specimens of the Hudson Highlands, New York. Zircon grains often display significantly greater age ranges, sometimes exceeding 1 b.y. (e.g., Valley et al., 2005, 2014). Deducing relationships between geologic events and zones in dated minerals, as well as internal consistency, is therefore critical to evaluating the significance of the zones and in compiling and comparing geochronological data from different localities.

However, very few mineral species can be dated by radiometric techniques. In some cases the mineral of interest is associated with a mineral species that can be dated, for example, the ages of many Be minerals depend on associated phases, such as beryl associated with biotite and muscovite dated by $^{40}\text{Ar}/^{39}\text{Ar}$ laser spot and step-heating measurements (Cheilletz et al., 1993) or Be minerals associated with columbite-tantalite dated by U-Pb measurements in pegmatite (e.g., Romer and Smeds, 1994; Breaks et al., 2005). Nonetheless, such age determinations can be problematic because evaluation of the age depends on inferences regarding the relationship of the dated mineral to the mineral of interest. Beryllium minerals often occur as metamorphic phases or as veins and thus appear to be younger than their host rocks (Grew and Hazen, 2014). In other instances, including detrital, supergene, or oxidized and weathered mineral phases, ages of mineral species remain indeterminate. The mineral age data we record in Table 1 thus reflect critical analysis of both the geochronological methods employed and the geological and petrological context of individual mineralized localities and their reported mineral species.

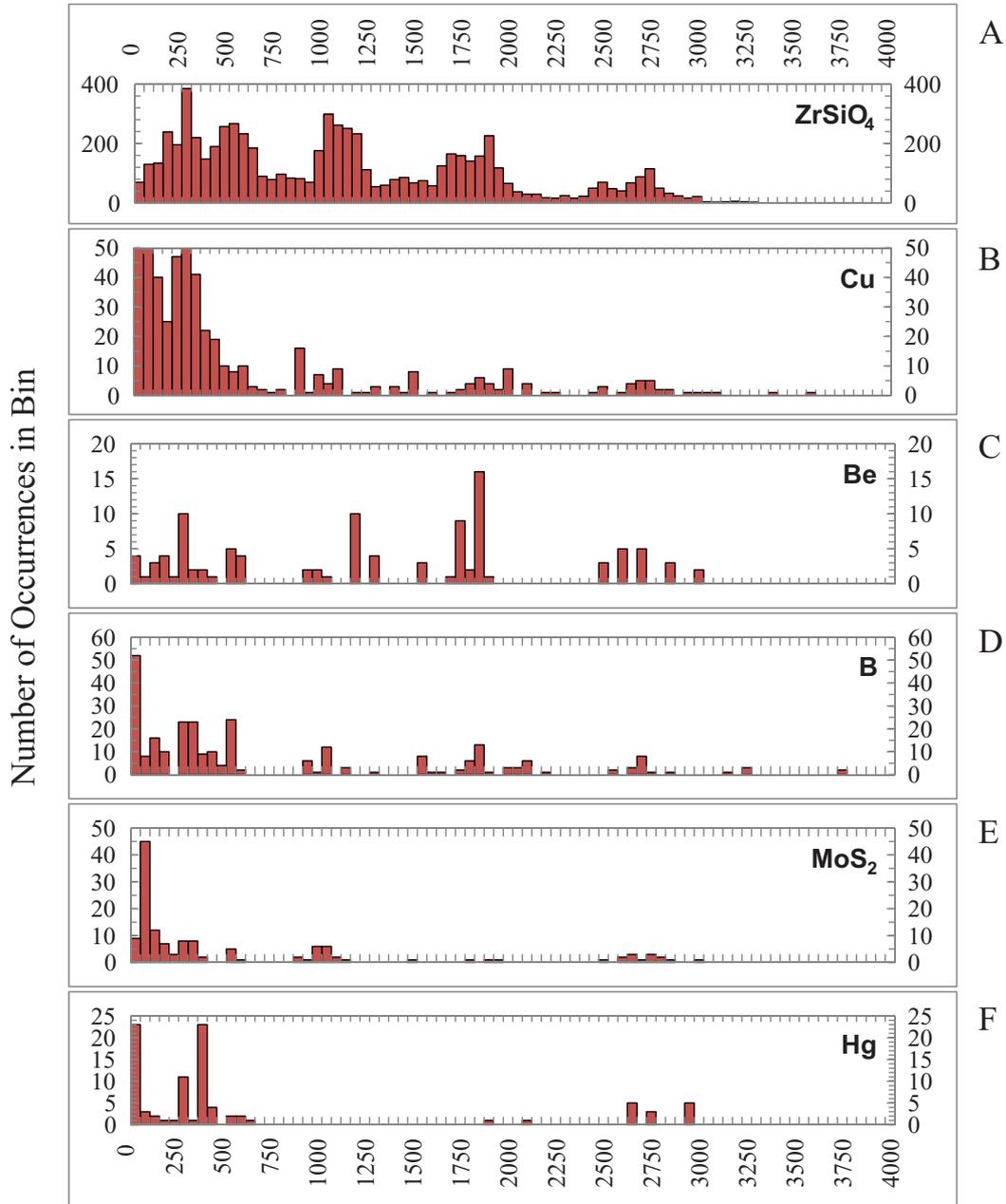


FIG. 1. Histograms of the secular variation of minerals in 50 Ma bins. A. Representative zircon temporal distributions (after Hawkesworth et al., 2010). B. Ages of 688 terrestrial localities of copper minerals (note that the 0–50 and 50–100 Ma bins have been truncated). C. First appearances of 106 mineral species of Be (Grew and Hazen, 2013, 2014). D. First appearances of 270 mineral species of boron (Grew and Hazen, 2010a, b; Grew et al., 2011). E. Ages of 136 terrestrial molybdenite (MoS_2) localities (Golden et al., 2013). F. Ages of the first appearances of 89 mineral species of mercury (Hazen et al., 2012).

Zircon

Dating individual grains of zircon can provide ages of processes associated with the growth and assembly of continents, such as magmatic activity and metamorphism, as well as associated mineralization. Thus, the temporal distribution of detrital zircon crystals can serve as a baseline for mineral episodicity associated with crustal evolution, as well as providing a standard of comparison for the secular variations observed for varied lithologies, ore deposits, minerals, and elements.

Zircon is suitable in this regard for at least six reasons: (1) zircon grains occur in large numbers in most detrital environments and thus provide statistically significant samples of temporal distributions; (2) zircon crystals invariably incorporate uranium and thus can be individually dated using U-Pb isotopes, although it should be noted that many grains display complex zoning that may represent more than a billion years of reworking; (3) zircon grains are mechanically robust and chemically resistant, and thus are minimally affected by

alteration in a sedimentary environment—the signature for U-Pb ages can also survive high-grade metamorphism; (4) zircon grains are released by the weathering of a variety of crustal lithologies and thus can sample a range of crustal processes through more than 4 b.y. of Earth history; (5) zircon has no known biological interactions, nor is Zr a redox-sensitive element, therefore, zircon provides a mineralogical baseline that is presumably unbiased by the evolving biosphere; and (6) the zircon record extends back at least 4400 Ma, older than any other known terrestrial mineral species (Cavosie et al., 2007; Harrison, 2009; Papineau, 2010; Valley et al., 2014). Zircon has the added advantage that its trace elements, isotopes, and fluid and mineral inclusions can potentially reveal details regarding the ancient environments in which they formed (Harley and Kelly, 2007; Scherer et al., 2007).

More than 3 b.y. of mineralogical episodicity has been observed for many thousands of individually dated zircon grains (Valley et al., 2005; Campbell and Allen, 2008; Rino et al., 2008; Condie and Aster, 2010; Hawkesworth et al., 2010; Bradley, 2011; Condie et al., 2011; Voice et al., 2011; Fig. 1A). Principal features of compilations of zircon secular variations are typically six or more peaks, each representing intervals of enhanced zircon crystallization and/or survival, notably at approximately 2700, 1850, 1050, 600, 400, and 175 Ma. For example, Condie and Aster (2010) synthesized data for ~40,000 zircon grains and identified several statistically significant peaks, the most prominent of which occur at 2700, 1870, 1000, 600, and 300 Ma. Similarly, Bradley (2011; fig. 16) tabulated more than 26,000 zircon ages and reported maxima at 2697, 1824, 1047, 594, 432, and 174 Ma, with lesser peaks at 2500 and 1435 Ma. Minima at 2347, 1565, 1371, 853, 529, and 367 Ma separate these peaks. The generally accepted interpretation of this episodicity is that zircon forms most abundantly and is most easily preserved in the continental

rock record, during the assembly of supercontinents, either through collisional orogenesis or marginal subduction. In particular, the maxima at approximately 2700, 1800, 1000, 600, and 400 Ma correspond to the assemblies of Kenorland, Nuna, Rodinia, Pannotia, and Pangaea, respectively (Table 2). [Note that we employ supercontinent names as proposed by Hoffman (1997), instead of the geographically distinct Superia/Scavia (Bleeker, 2003; Cawood et al., 2013) and Columbia (Rogers and Santosh, 2002), which have also been proposed for the oldest supercontinents, and Pannotia instead of Gondwana (cf. Hazen et al., 2012).]

Inasmuch as the process of supercontinent assembly ultimately halts the convergence of continents by which it formed, zircon crystallization might be assumed to decline significantly once a supercontinent has entered its period of stability. Minima in Figure 1A have thus been ascribed to these intervals of relative quiescence. The observed distributions of zircon ages thus reflect secular changes in tectonic boundaries and may not be primarily a function of preservational bias, except in the sense that the encased cores of orogenic belts are relatively protected from subsequent recycling at plate margins (Cawood and Hawkesworth, 2013). In this context zircon ages can provide an important reference frame by which other episodic mineralization patterns can be understood.

Copper minerals

The Mineral Evolution Database (Hazen et al., 2011) currently records ages for 688 mineral districts (representing ~3,000 specific localities in the mindat.org database) with copper minerals (as of January 2014), based largely on the compilations of Cox et al. (2003) and Singer et al. (2005, 2008). Though only a small fraction of the more than 50,000 Cu localities recorded by mindat.org, these preliminary results suggest episodicity in copper mineralization (Fig. 1B). Maxima at

TABLE 2. Chronological Overview of the Supercontinent Cycle and Temporal Distributions of Mineral Species

Name	Status	Interval (Ma)	Duration (Ma)	No. of mineral localities or new species				
				Cu ¹	Be ²	B ³	Mo ⁴	Hg ⁵
Ur/Vaalbara	Uncertain	>2800		8	5	7	2	2
Kenorland	Assembly	2800–2500	300	17	13	14	11	6
	Stable	2500–2200	300	5	0	0	0	0
	Breakup	2200–1900	300	16	0	13	0	1
Nuna	Assembly	1900–1700	200	16	28	22	3	4
	Stable	1700–1400	300	11	4	10	1	0
	Breakup	1400–1200	200	7	4	1	0	0
Rodinia	Assembly	1200–1000	200	14	11	15	9	0
	Stable	1000–750	250	26	4	7	9	4
	Breakup	750–600	150	6	0	0	0	1
Pannotia	Assembly	600–500	100	18	9	26	4	5
	Stable	500–430	70	20	1	8	0	4
Pangea	Assembly	430–250	180	13	14	61	18	29
	Stable	250–175	75	60	5	5	4	7
Cenozoic ⁶	Breakup	175–65	110	72	3	24	41	13
		65–present	65	359	5	57	29	50

¹ Ages of 688 copper mineral localities

² First appearances of 106 Be mineral species, after Grew and Hazen (2014)

³ First appearances of 270 B mineral species, after Grew and Hazen (2010b)

⁴ Ages of 136 molybdenite localities (Golden et al., 2013)

⁵ Ages of 126 Hg mineral localities (Hazen et al., 2012)

⁶ The last 65 m.y. have been characterized by simultaneous continental rifting and convergence

~2750, 1850, 1000, and 300 Ma echo well-established zircon peaks, as do periods of fewer Cu localities at ~2350, 1600, and 850 Ma.

However, there are also important differences between the temporal distribution of Cu minerals and the zircon record (David Huston, pers. commun., 2014). For example, data from the Zambian copper belt and similar deposits in Australia point to significant mineralization at ~830 Ma. Other notable Cu deposits, as well as unconformity related U deposits and sediment-hosted Zn deposits in Australia and Canada, formed between 1690 and 1575 Ma. These and other episodes point to significant metallogenesis not associated with supercontinent assembly.

The most notable deviation in the temporal distribution of copper localities compared to zircon is the large number of localities recorded for the Phanerozoic eon (<543 Ma) and, particularly, the Cenozoic Era (<65.5 Ma). This recent maximum in Cu mineralization is biased by the inclusion of numerous porphyry copper localities (Singer et al., 2005, 2008), which would be among the first deposits lost during orogenesis, and thus are disproportionately represented in more recent formations

Changes in the nature and extent of Cu mineralization are also associated with the evolution of redox-controlled copper deposition mediated by the biosphere. Prior to the Great Oxidation Event (GOE; ~2200 Ma), near-surface oxygen fugacity was sufficiently low that copper would not have occurred in its divalent state (Hazen et al., 2013a). Thus, most known copper minerals could not have formed, and extensive Cu mineralization was restricted to no more than ~13 minerals, including sulfides and native Cu (Hazen, 2013). Surface oxidation to Cu^{2+} was possible after atmospheric oxygenation, but subsurface conditions consistent with Cu ore deposition through redox processes may have postdated the Great Oxidation Event by as much as 1 b.y. (Golden et al., 2013). Thus, copper mineralization, and particularly the diversification of near-surface copper mineralogy, was primarily a consequence of changes in near-surface environments mediated by life.

Beryllium minerals

Grew and Hazen (2013, 2014) have compiled reports of the earliest, intermediate, and most recent occurrences in the geologic record of 106 species of beryllium minerals (Table 2; Fig. 1C). Though these age data are sparse compared to the data obtained on zircon, significant secular trends related to the supercontinent cycle emerge. In particular, we observe maxima in the number of earliest occurrences of Be minerals at 2700 to 2600, 1850 to 1750, 1050 to 950, 600 to 550, and 300 Ma—all times of presumed supercontinent assembly. These pulses of Be mineral diversification closely follow the secular trend for ages of granitic pegmatites tabulated by Tkachev (2011), who reported the five greatest maxima at ~2600, 1750, 950, 525, and 350 Ma (as well as varying temporal trends for different classes of pegmatites, which he attributed to Earth's gradual cooling). Note that these time intervals for both Be minerals and granitic pegmatites lag behind the corresponding zircon peaks by as much as ~50 to 100 Ma. It is thus tempting to suggest that differentiation of granitic magma sufficient for the requisite enrichment of rare elements, for example enrichment of Be to precipitate

Be minerals, might require up to 50 to 100 Ma after crystallization of granite as dated by zircon. However, in most cases when individual granite-pegmatite systems are considered, a much shorter lag is found; for example, Grew and Hazen (2014) concluded a reasonable estimate is ~15 Ma for the Black Hills, South Dakota, and Swanson (2012) gave ~0 Ma in the tin-spodumene belt along the North Carolina-South Carolina border.

Pulses of Be mineral diversification are associated not only with episodes of supercontinent assembly but also with peralkaline complexes, where the Be minerals are found largely in pegmatites and veins. Premier examples are the Ilímaussaq (e.g., Markl, 2001) and Igaliko complexes, respectively 1160 and 1270 Ma in age (Krumrei et al., 2006; McCreath et al., 2012), in the Gardar province of southwest Greenland. This igneous activity occurred during continental rifting, which Grew and Hazen (2014) conjectured could bear a relationship to the older events in the Grenville belt analogous to that of far-field rifting in the Oslo graben to the Variscan/Hercynian orogeny. Alternatively, the rifting could be related to the postulated rotation of Baltica with respect to Laurentia between >1265 and <1000 Ma, which also created an ocean basin, the Asgard Sea (Cawood et al., 2010). Nineteen Be minerals have been reported from Ilímaussaq and Igaliko, of which 14 are earliest known occurrences in the geologic record. Phanerozoic alkaline and peralkaline complexes can also host an equally diverse suite of Be minerals, but only a few of these species are unknown from earlier occurrences. Notable examples are the 294 Ma larvikite suite in the Oslo graben, Norway (26 total and three new Be minerals; Larsen, 2010), and the 124 Ma (Gilbert and Foland, 1986) Mont Saint-Hilaire complex, a part of the province of the Monteregian Hills near Montreal, Quebec, Canada (19 total and two new Be minerals; e.g., Horváth and Horváth-Pfenninger, 2000).

Note that beryllium is not redox-sensitive (it is found only in the Be^{2+} state), and Be plays no significant role in biology. Therefore, beryllium mineralization does not appear to have been influenced by changes in the biosphere. Therefore, with the exception of species such as bergslagite [$\text{CaBeAsO}_4(\text{OH})$], danalite [$\text{Be}_3(\text{Fe}^{2+})_4(\text{SiO}_4)_3\text{S}$], and trimmerite [$\text{CaBe}_3(\text{Mn}^{2+})_2(\text{SiO}_4)_3$] that also incorporate redox-sensitive elements, beryllium mineralization does not appear to have been significantly influenced by changes in the biosphere.

Boron minerals

Grew and Hazen (2010b) and Grew et al. (2011) presented a preliminary compilation of the earliest reported occurrences of 270 boron minerals in the geologic record (Table 2; Fig. 1D). These data reveal a pattern similar to that reported by Bradley (2011) for zircon ages. Prior to ~50 Ma, the six largest peaks in the first appearances of boron minerals are observed at ~2700, 1850, 1050, 550, 350, and 150 Ma. Thus, the role of supercontinent assembly that has been invoked in the temporal variation of zircon grains also appears to explain major variations in boron mineralogy prior to the last 50 Ma.

Three additional spikes of boron mineral diversification enrich the boron mineral evolution story. First, we observe nine new boron minerals in the interval from ~2100 to 2000 Ma, during the presumed breakup of Kenorland. Six of these minerals are metamorphic borates, e.g., ludwigite

[Mg₂Fe³⁺O₂(BO₃)] and suanite (Mg₂B₂O₅), the precursors of which were deposited between 2100 and 2400 Ma in evaporites hosted by sedimentary and volcanic rocks and metamorphosed at about 2000 Ma in the Liaoning-Jilin area of northeastern China (Zhang, 1988; Peng and Palmer, 1995, 2002). These deposits are located in the Paleoproterozoic Jiao-Liao-Ji belt, which lies at the eastern margin of the Eastern block of the North China craton (Zhao et al., 2005). According to Zhao et al. (2005), the tectonic nature of the Jiao-Liao-Ji belt has been controversial and two scenarios have been proposed: (1) continent-arc-continent collision and (2) an intracontinental rift along the eastern margin of the North China craton. However, Peng and Palmer (2002) interpreted the evaporitic borates as having been deposited in a postcollisional extensional setting between 2100 and 2400 Ma. The other three new B minerals are borosilicates, e.g., werdingite (Mg₂Al₁₄Si₄B₄O₃₇; Grew et al., 1997), from the Magondi belt near Karoi in northern Zimbabwe, in which sediments about 2200 to 2000 Ma in age were metamorphosed under granulite-facies conditions at 2000 Ma during assembly of Archean cratons into a large continent in West Africa and South America at a time when the converse was happening in North America and Fennoscandia, namely extension and breakup of Archean cratons (Master et al., 2010). That is, the 2100 to 2000 Ma spike in B mineral diversity appears to be indicative of continental assembly in the southern hemisphere and northern China that was coeval with the Kenorland breakup. Moreover, the 2100 to 2000 Ma spike coincides temporally to a peak in number of pegmatitic deposits that Tkachev (2011) reported was restricted to Gondwana block continents.

The second spike involves the first appearance of eight borates at ~1550 Ma during the breakup of the supercontinent of Nuna. Seven of these borates from the skarn deposits in contact aureoles of rapakivi granites at Pitkäranta, Lake Ladoga region, Karelia, Russia (Aleksandrov and Troneva, 2009) have ages of 1538 Ma (Stein et al., 2003). The rapakivi granites are intrusions that are 150 to 350 m.y. younger than the Svecofennian country rocks (Rämö and Haapala, 2005; Cawood and Hawkesworth, 2014), which would be related to assembly of Nuna. The eighth borate, chambersite (Mn₃B₇O₁₃Cl), occurs with dolostone deposited in a subtidal lagoon of an epicontinental sea at 1500 Ma on the North China platform (Fan et al., 1999; Shi et al., 2008).

Finally, 56 boron minerals are only known from the last 50 m.y. We attribute this recent spike in boron mineral diversity, which is not evident in the recent record of zircon or Be mineralization, to the preservation of ephemeral minerals, such as borax, colemanite, kernite, and other water soluble phases that are readily lost from the rock record. In this respect, the temporal distribution of the minerals of boron and other elements forming diverse suites in evaporites, fumaroles, and lagoons would differ from the distribution of zircon ages.

The role of boron in the history of the coevolving geosphere and biosphere is enigmatic. Benner and coworkers (Benner, 2004; Ricardo et al., 2004; Kim and Benner, 2010; see also Prieur, 2001; Scorei and Cimpoiăsu, 2006) have suggested that borate minerals could have played a unique and possibly essential role in life's origins as templates for RNA assembly. However, Grew et al. (2011) challenged the assumption that

borate minerals were widely available in the Hadean Eon or Paleoproterozoic Era, prior to biogenesis. Thus, the earliest appearance of evaporite boron minerals continues to be a matter of significant interest and study.

Molybdenite episodicity

Golden et al. (2013) reported data on ages of 136 molybdenite localities, which reveal episodicity with statistically significant pulses of mineralization at 2800 to 2500, 1900 to 1780, 1060 to 910, 560 to 510, and 380 to 250 Ma (Table 2; Fig. 1E). Though data are few prior to the Neoproterozoic era (1000–542 Ma), these ages fit to four statistically significant Gaussian curves with maxima at 2704 ± 24, 998 ± 13, 548 ± 17, and 304 ± 7 Ma. Additionally, three localities cluster in ages between 1900 to 1790 Ma but are insufficient to define a peak. These five periods of maximum molybdenite mineralization are separated by temporal gaps at 2500 to 1900 Ma (no recorded localities), 1780 to 1060 Ma (2 recorded localities), 910 to 560 Ma (no recorded localities), and 510 to 380 Ma (no recorded localities).

A caveat is required with respect to compiling ages of mineral localities, as opposed to first appearances of minerals cited above for Be and B. We define a “locality” as a mineral-producing location with a distinct age. However, in some cases several localities occur in close spatial and temporal proximity and thus probably represent a single well-prospected mineralized district. For example, eight Norwegian Mo mining localities, including Sira, Gursil, and Vardal with ages from 988 to 916 Ma, are listed separately in Table 2 and Figure 1D, but are likely to be genetically related. Thus, Neoproterozoic molybdenum mineralization at ~950 Ma is disproportionately represented in our analysis. Similarly, dozens of separate Mesozoic and early Cenozoic mines, primarily in porphyry-related plutons from Mo-bearing districts of China, Japan, Mexico, and Bulgaria-Romania-Serbia are listed separately, but probably represent fewer distinct mineralized districts.

Nevertheless, the secular variation of molybdenite mineralization conforms almost exactly to the maxima observed for zircon ages and would appear to reflect a similar close relationship to intervals of supercontinent assembly. It is remarkable that 98% of these molybdenite localities occur in time intervals representing less than 40% of the past 3 b.y.. Thus, most 50-m.y. time bins in Figure 1D have no reported molybdenite localities.

The coevolution of molybdenum minerals and biology is of special interest. Not only is Mo a redox-sensitive element, but it also plays an important biological role, for example in the nitrogenase enzyme that facilitates conversion of inert N₂ to biologically active ammonia (Zehr and Ward, 2002; Rees et al., 2005; Schwartz et al., 2009; Kim et al., 2013). In its more reduced Mo⁴⁺ form, molybdenum is insoluble; therefore, the relatively reducing ocean prior to the Great Oxidation Event was presumably poor in molybdenum, while being correspondingly enriched in Fe²⁺. Accordingly, the most ancient (i.e., phylogenetically “deeply rooted”) nitrogenase enzymes use only iron in their active sites. By contrast, after the Great Oxidation Event oceans gradually became more oxidizing, and thus were enriched in soluble Mo⁶⁺ (eventually to >10 parts per billion [ppb]; Emsley, 1991). At the same time, oceans were depleted in iron (to <1 ppb), which was deposited as

Fe³⁺ minerals in banded iron formations. Therefore, more recently evolved nitrogenase enzymes typically incorporate Mo as well as Fe in their active sites. In this way the metal contents of microbial enzymes reflect the ancient molybdenum cycle and other changes in ocean chemistry that were, themselves, largely a consequence of oxygenic photosynthesis (David and Alm, 2011).

Mineral evolution studies that focus on trace and minor element chemistry may reflect biologically mediated changes in Earth's near-surface redox state. For example, rhenium, a trace element that is invariably incorporated into molybdenite, is insoluble in its Re⁴⁺ state, but soluble in its more oxidized Re⁷⁺ state. Accordingly, Golden et al. (2013) predicted that the Re content of molybdenite should display a significant increase after the Great Oxidation Event. They gathered age and Re composition data for 422 molybdenite samples spanning 3 b.y., and reported a significant increase in the average trace element rhenium content in molybdenite, from 71 ppm in 49 Archean Eon specimens to 589 ppm in 82 Cenozoic Era specimens. Golden et al. (2013) interpreted this significant increase as a consequence of biologically induced near-surface oxidation.

Mercury minerals

Hazen et al. (2012) surveyed the first appearances and distribution of 89 species of mercury minerals (126 Hg mineral localities) through time and reported statistically significant episodic trends (Table 2; Fig. 1F). They fit their data to five Gaussian curves with the following means \pm standard deviations: 2690 \pm 40, 1810 \pm 50, 530 \pm 50, 320 \pm 7, and 50 \pm 50 Ma. In sharp contrast to these more active periods of widespread Hg mineral formation, they recorded significant intervals of minimal mercury mineralization during the periods ~2500 to 2000, 1800 to 600, and 250 to 65 Ma. Significant pulses of mercury mineralization thus occurred during the assemblies of Kenorland, Nuna, Pannotia, and Pangaea—patterns consistent with those observed for zircon and molybdenite, as well as the minerals of B, Be, and Cu.

In contrast, Hg mineralization during the late Paleoproterozoic and Neoproterozoic Eras appears to differ significantly from the zircon record. No new mercury mineral species, and only four Hg mineral localities (all from 800–600 Ma), have been reported for the 1.2-billion year period from 1800 to 600 Ma—an interval that encompasses the assembly of Rodinia. This period is notable for the possible influence of sulfate-reducing microbes and the resultant sulfidic “intermediate ocean” (Canfield, 1998; Anbar and Knoll, 2002; Poulton et al., 2004; Poulton and Canfield, 2011). Hazen et al. (2012) thus suggested that this hiatus in Hg mineralization reflects the sequestration of Hg as nanoparticles of cinnabar in a sulfidic Proterozoic ocean. However, subsequent investigations of Mesoproterozoic marine black shales (in progress and as yet unpublished) have not revealed the requisite concentrations of Hg associated with this proposed mode of Hg sequestration.

Alternatively, the tectonic setting of Rodinian assembly may have differed from that of other supercontinents—a contrast that could have affected metallogeny (Cawood et al., 2009; Huston et al., 2010; Pehrsson et al., 2013; Cawood and Hawkesworth, 2014). Huston et al. (2010) suggested that

the assembly of Rodinia was tectonically distinct in that it was “dominated by advancing accretionary orogenesis” and a corresponding paucity of volcanic-hosted massive sulfide (VHMS) deposits compared to other intervals of supercontinent assembly. Back-arc basin formation was thus inhibited. It is possible that submarine volcanics may have been removed by subductive erosion, but Cawood and Hawkesworth (2014) suggested that accretionary rocks along the margin of Laurentia/Baltica argue against significant erosion. The observed temporal gap in Hg mineralization might thus be related to the decline in VHMS deposits documented by Huston et al. (2010). Cawood and Hawkesworth (2014) documented other distinctive characteristics of the interval from 1700 to 750 Ma, including: (1) the near absence of passive margins; (2) a lack of orogenic gold and VHMS deposits, iron formations, and glacial deposits; (3) a pulse of anorthosite formation; and (4) significant Mo and Cu mineralization, including the world's largest known deposits of these metals. However, the reasons for the altered Hg cycle during this time interval remain a matter of ongoing study.

As in the case of boron minerals, we observe a recent pulse of Hg mineral localities and new mercury minerals (45 of 127 localities within the past 50 Ma). This increase may in part reflect a striking influence of the terrestrial biosphere: Hg is effectively concentrated by relatively weak bonding to buried organic matter, from which mercury is easily remobilized by subsequent interaction with hydrothermal fluids. Many of Earth's major Hg ore deposits coincide with the formation of Carboniferous coal measures. This interval, which also saw a tripling of the number of observed Hg mineral species, may thus reflect biological perturbations of the mercury cycle.

Finally, a pulse of Hg mineral deposits and diversity during the past 30 m.y. may also reflect preservational bias; a number of ephemeral mercury minerals (including native Hg) gradually evaporate under atmospheric conditions. In addition, several rare mercury minerals are known only from ore dumps and smelter by-products, and thus may represent anthropogenic paragenesis.

Possible Origins of Episodic Metallogenesis

Geologists have long recognized that ages of crustal rocks and minerals, including ore deposits, reveal intervals of maximum and minimum formation through more than 3 b.y. of Earth history (Gastil, 1960; Laznicka, 1973; Anhaeusser, 1981; Meyer, 1981, 1985, 1988; Rundqvist, 1982; Domarev, 1984; Goldfarb et al., 2001; Groves et al., 2005, 2010; Kerrich et al., 2005; Rino et al., 2008; Condie and Aster, 2010; Hawkesworth et al., 2010; Huston et al., 2010; Iizuka et al., 2010; Condie, 2011; Hazen et al., 2012; Arndt, 2013; Cawood and Hawkesworth, 2013; Golden et al., 2013; Pehrsson et al., 2013; Kaur and Chaudri, 2014; Grew and Hazen, 2014). Two possibly complementary explanations have been offered for such episodicity: (1) enhanced mineral formation and/or preservation related to the supercontinent cycle; and (2) enhanced crustal formation related to nonuniform plate tectonics, including periodic mantle superplumes (Condie, 1998), episodic subduction related to slab “avalanches” (Stein and Hoffman, 1994), and intervals during which plate motions and subduction accelerate (Silver and Behn, 2008; O'Neill et al., 2009; Dhuime et al., 2012).

Supercontinent cycles and episodic preservation

Varied lines of evidence taken from paleontological, paleotectonic, geologic, and geomagnetic investigations reveal a quasi-periodic cycle of assembly and dispersal of Earth's continents. This supercontinent cycle, which has persisted for at least the last 2.8 b.y., and may extend back >3.2 b.y. (Worsley et al., 1986; Gurnis, 1988; Nance et al., 1988, 2014; Rogers and Santosh, 2002, 2004, 2009; Zhao et al., 2004, 2005; Condie et al., 2009; Murphy et al., 2009; Santosh et al., 2009; Bradley, 2011; Meert, 2012), ideally features a sequence of three global tectonic processes. The first stage of continental aggregation is characterized by convergence, continental collision, and associated orogenic events. Such periods of continental assembly saw the emergence of modern Earth's largest mountain chains, including the Himalayas, the Alps, the Urals, and the Appalachians, and may have been times of enhanced production of continental crust. However, some models show that overall crustal growth has been continuous albeit variable over geologic time, generally decreasing after 3000 to 2500 Ma (Belousova et al., 2010; Dhuime et al., 2012). The cycle's second stage encompasses periods of stable aggregation of most of Earth's landmass, during which supercontinents experience marginal subduction of oceanic crust and associated near-coastal acidic volcanism. The third stage of the idealized supercontinent cycle includes continental rifting and breakup, the formation of new ocean basins, and ultimately maximum dispersal of several continents.

The three stages of the supercontinent cycle—assembly, stability, and breakup—typically overlap, because all three modes of tectonic activity may occur simultaneously at different regions of the globe (as they do today). It is thus difficult to provide an exact 3-billion year chronology for Earth's supercontinent cycle. Rogers and Santosh (2004, 2009) used the concept of “maximum packing” of supercontinents for the situation when a single landmass includes the greatest amount of available continental lithosphere. In this context, five well-defined episodes of supercontinent formation or maximum packing, dating to ~2.8 b.y. ago, have been proposed (e.g., Cheney, 1996; Rogers, 1996; Rogers and Santosh, 2002; Bleeker, 2003; Pesonen et al., 2003; Zhao et al., 2004; Hou et al., 2008; Li et al., 2008; Bogdanova et al., 2009; Bradley, 2011; Meert, 2012; Nance et al., 2014; Table 2).

Uncertainties remain regarding the timing and extent of supercontinent formation throughout the past 3500 Ma. Some authors have suggested the occurrence of one or two intervals prior to 2800 Ma, named variously as Ur and/or Vaalbara (e.g., Cheney, 1996; Zegers et al., 1998; Rogers and Santosh, 2003, 2004; Nance et al., 2014). Given the paucity of mineral data from >3000 Ma, we do not treat this possibility in our survey.

Continued debate also surrounds the nature of the late Neoproterozoic supercontinent associated with global “Pan-African” events, which led to the formation of Gondwana (Unrug, 1992; Meert and Van Der Voo, 1997), and Gondwana's subsequent brief convergence with Laurentia to form Pannotia (Dalziel, 1991, 2013; Stump, 1992; Cawood et al., 2001) in the early Cambrian Period. Simultaneous episodes of convergence and rifting during the 200 Ma prior to the assembly of Pangaea underscore the complexities of the supercontinent “cycle” and force us to make compromises in

our choices for the global chronology to be adopted in this review. Thus, we will assume an interval of Pannotia assembly at ~600 to 500 Ma, followed by a period of maximum aggregation at ~500 to 430 Ma, prior to Pangaea assembly (Table 2; cf. Santosh et al., 2009; Nance et al., 2014). The durations of other stages listed in Table 2 are distilled from different papers that provide a range of ages—a situation that reflects that the stages of the supercontinent cycle overlap and cannot be assigned exact global ages.

Episodic plate tectonics

A number of authors have argued against the role of supercontinent assembly and enhanced crustal preservation in the episodicity of metallogenesis (e.g., Arndt, 2013, and references therein). These authors point to poor correlations between the ages and the greater than 100-million year durations of presumed periods of supercontinent assembly on the one hand, and relatively sharp (<10-m.y. duration) maxima in the age distributions of minerals (especially detrital zircon) on the other. In other words, if mineral paragenesis is strongly correlated with supercontinent assembly then one might expect broader maxima in the age distributions of zircon and other minerals. An alternative explanation is that periodicity in crustal ages is correlated with mantle plumes and episodic mantle convection (Stein and Hoffman, 1994). Details of trace element and isotope distributions in many granitic terranes associated with these maxima may point to an origin via subduction rather than in collisional orogenies (Arndt, 2013).

On the relative intensity of mineralization events

If each supercontinent cycle resulted in a similar degree of continental crust formation and associated mineralization, then one might expect the abundances of episodic features (i.e., numbers of mineral grains or numbers of localities) to display a systematic increase closer to the present day as a consequence of subduction, erosional loss, and other preservational biases. However, this increasing trend is not generally found—a result that may point to a greater extent of continental crust formation and preservation during the Archean Eon and Paleoproterozoic Era compared to later periods. For example, the zircon record, though strongly influenced by regional sampling biases that focus on the most accessible and economically productive ancient cratonic systems (Condie and Aster, 2010; Hawkesworth et al., 2010), shows that there are more detrital zircon grains of ages associated with the ~1850 Ma assembly of Nuna than with the subsequent 950 Ma assembly of Rodinia (Condie and Aster, 2010; Bradley, 2011; Condie et al., 2011). A similar situation is observed for the minerals of mercury, which are uncommon in rocks of Neoproterozoic age. However, as noted previously, several authors have suggested that the period of Rodinian assembly was distinctive in its tectonic setting and consequent mineralization (Cawood et al., 2009; Huston et al., 2010; Pehrsson et al., 2013; Cawood and Hawkesworth, 2014).

A comparison of mineralization between the Archean and Proterozoic Eons displays similar trends. More molybdenite and mercury localities and a greater abundance of detrital zircons are associated with the ~2800 Ma assembly of Kenorland in the Archean Eon than with assembly of the Proterozoic supercontinent of Nuna—a trend that is also reflected

in the greater intensity of crustal magmatism at 2700 compared to 1900 Ma (Balashov and Glaznev, 2006), though the prevalence of granitic pegmatites does not follow this trend (Tkachev, 2011, fig. 3).

Note, however, that zircon data may point to the importance of regional effects in the magnitude of the 2700 Ma peak; different maxima and peak ages are observed for subsets of samples from the Superior province in Canada, versus those in southwestern Australia, western Superior province, and Karelia (Condie et al., 2009; Condie and Aster, 2010; although see Voice et al., 2011). Nevertheless, a worldwide cluster of zircon ages at ~2700 Ma is a dominant feature in several zircon age compilations and thus represents a significant global crystallization and preservation of zircon grains from that period. Accordingly, Condie and Aster (2010) estimated that ~80% of juvenile continental crust, and a corresponding percentage of the detrital zircon record, was produced prior to 1650 Ma, consistent with an estimate based on a model integrating crustal generation and reworking rates (Dhuime et al., 2012).

Discussion

The temporal distributions of the minerals of Be, B, Cu, Hg, and Mo reveal episodicity, with a significant correlation of metallogenesis during episodes of supercontinent assembly. However, whereas the first-order pattern of episodicity recorded in this and numerous other studies is generally consistent and suggests global-scale cyclic tectonic patterns, distinctive trends in the timing and intensity of mineralization are emerging. These preliminary data thus point to a number of unanswered questions that can inform future studies of the secular variations of mineral diversity and deposition.

Why is mineral diversity (and metallization) relatively low in the Archean Eon?

Hazen et al. (2008) suggested that as many as 1,500 mineral species are possible on a nonliving Earth-like planet (with more than 3,000 additional species arising as a consequence of biologically mediated changes, notably atmospheric oxygenation, in Earth's near-surface environment). Nevertheless, far fewer mineral species—possibly fewer than 500—are found in rocks older than 3500 Ma. Three possible causes have been cited for this observed mineralogical parsimony of the Archean and, presumably, the Hadean Eons. The first possibility is that mineral diversity was inherently low, perhaps restricted to no more than about 420 widespread and volumetrically significant phases (Hazen et al., 2008; Hazen, 2013). In this case, elapsed time for crustal evolution was insufficient for the selection and concentration of rare elements, including most ore-forming metals. If this scenario is correct, and more than 1 b.y. of fluid-rock interactions were required to produce significant metal deposits in Earth's crust, then we predict a similarly restricted mineralogical diversity on the smaller and more rapidly cooling Mars, which would have experienced correspondingly less fluid-rock interactions and associated mineralogical diversification.

A second possibility is that extensive and diverse mineral deposits formed during Earth's Hadean Eon and Paleoproterozoic Era, but much of this ancient crust was subsequently destroyed (an exception being the Isua supracrustal belt in southwest Greenland). At least two modes of Hadean/early

Archean crustal destruction have been proposed. On the one hand, extensive bombardment by tens of thousands of meteor and comet impacts >1 km in diameter (Marchi et al. 2012, 2013a; Morbidelli et al., 2012) may have largely melted and otherwise destroyed the earliest crust. Marchi et al. (2013b; pers. commun., 2013) estimate that the average crustal surface was disrupted at least twice during this interval, and observations of shocked detrital grains of Hadean and Paleoproterozoic age lend support to the widespread destructive consequences of impacts (Cavosie et al., 2010; Erickson et al., 2013).

Alternatively, a second possible distinctive mode of Hadean and early Archean crustal destruction is via crustal delamination. It has been proposed that crust-forming processes in the Hadean and early Archean Eons were the consequence of mantle plumes and thus differed significantly from subduction-mediated crustal evolution (Stein and Hoffman, 1994; Arndt, 2013). The resulting predominantly mafic Archean crust may have been denser than the underlying mantle, and thus gravitationally unstable (Herzberg, 2014; Johnson et al., 2014), leading to crustal delamination and destruction of much of Earth's crust, and much of the associated mineral diversity, formed during the first billion years. Note also that an undifferentiated mafic crust would have been inherently less diverse mineralogically than a more evolved felsic crust.

Whereas low inherent mineral diversity and/or contemporaneous crustal destruction remain speculative reasons for the observed mineralogical parsimony of Hadean and early Archean rocks, very little of which remains (e.g., Hawkesworth et al., 2013), the third mode of Hadean/Archean crust loss—gradual erosion over the past 3.5 b.y. of Earth history—has undoubtedly contributed, as well. Rates of Hadean erosion are uncertain. On the one hand, postulated high atmospheric CO₂ may have enhanced subaerial weathering (Walker et al., 1981; Rye et al., 1995; Sagan and Chyba, 1997; Kauffman and Xiao, 2003; Ohmoto et al., 2004). However, rates of erosion may have been moderated by the presumed relatively low topographic relief during the Hadean Eon, when a hot and correspondingly weak lithosphere could not have supported crustal loads associated with high topography (Rey and Coltice, 2008). Indeed, it may not have been until the Neoproterozoic Era that continental topography began to approach modern extremes, with associated enhanced hydrological weathering (Kump and Barley, 2007; Campbell and Allen, 2008).

One possible observational approach to resolving the question of the extent of Hadean/Archean mineral diversity and modes of crustal loss is a closer examination of suites of dense detrital minerals in Earth's oldest sediments. Understandably, much focus has been directed at zircon and monazite, in large measure because ages can be obtained for individual grains. However, dozens of other potential heavy minerals might reveal clues regarding the early crust. For example, cassiterite (SnO₂) occurs in medium- to high-temperature hydrothermal veins and pegmatites associated with granite intrusions and is commonly preserved as detrital grains. At present, the oldest reported cassiterite deposits are the 3000 Ma Sinceni pluton, Kaapvaal craton, Swaziland (Trumbull, 1995), and 2850 Ma tin-bearing granites in the Pilbara craton of Western Australia (Kinny, 2000; Sweetapple and Collins, 2002). The discovery of detrital cassiterite in sediments significantly older than 3 b.y. old would point to tin

mineralization (and subsequent erosional loss) much earlier than known in situ deposits.

What is the geologic context of each deposit?

It is difficult to integrate data on a given mineral or chemical element without considering the detailed geologic and lithologic context of the host deposit. For example, Tkachev (2011) investigated the episodicity of granitic pegmatites and documented distinct temporal trends for different pegmatite classes. Only rare metal pegmatites appear throughout the interval from the Archean into the Phanerozoic Eon. By contrast, muscovite pegmatites and miarolitic pegmatites do not first appear until the Paleoproterozoic and Mesoproterozoic Eras, respectively. An understanding of geologic context is particularly important in studies of the first occurrences of minerals in the geologic record.

Grew and Hazen (2013, 2014) emphasized this critical need to consider geologic context in interpreting the diversification of beryllium minerals. For example, a spike in diversity in the ~1800 to 1850 Ma Långban-type deposits of the Bergslagen ore region of central Sweden resulted from metamorphism of a mixture of elements not often found together, whereas spikes in diversity of pegmatitic minerals are often due to low-temperature alteration of primary minerals. Indeed, the fact that almost half of all known Be minerals are recorded from only one known locality suggests that contingency plays a significant role in the occurrence of rare mineral species (Grew and Hazen, 2014). Extending this approach to the minerals of other elements thus represents an important opportunity for future research.

What are the paleotectonic settings of mineral localities?

An obvious missing piece of the mineral evolution story thus far is the correlation of locality and age information with paleotectonic settings—in particular proximity to known active paleoplate boundaries. An effective example of this kind of reconstruction is provided by Kaur and Chaudhri (2014) for the ~1850 Ma Paleo-Mesoproterozoic supercontinent Nuna. They display the spatial relationship of various metal deposits with presumed marginal subduction zones; however many more deposits could be added to their compilation. Work in progress will attempt to present similar visualizations for other supercontinents, which might help to clarify the roles of tectonic processes in mineralization.

What role does preservational bias play in the observed trends?

After reviewing the sequence of 12 nonferrous metals, including Cu, Mo, and Hg, Laznicka (1973) concluded that depth of denudation is more important than conditions of formation and their progressive evolution in determining the age relationships of ore deposits presently exposed at Earth's surface. However, it has been proposed that zircon data, if properly corrected for regional sampling biases, can provide a relatively accurate view of the scale and temporal distribution of granitic magmatism and juvenile continent formation (Condie and Aster, 2010; Hawkesworth et al., 2010; Bradley, 2011). Even if that supposition is true, it is still unclear the extent to which preservational bias affects the record of other less robust minerals and chemical elements. In contrast to

zircon, the problems associated with ephemeral phases, such as many minerals of boron, copper, and mercury, are evident from the disproportionate Cenozoic record of those minerals. Similarly, the record of clay mineral evolution on Earth has been largely erased by subduction and various near-surface processes (Hazen et al., 2013b).

Therefore, we need to develop a more comprehensive survey of the areal distribution of rocks of different ages, coupled with their lithologic, metamorphic, and tectonic context, in order to establish preservational baselines (Hazen et al., 2011). This proposed large-scale effort is analogous to the Paleobiology Database (<http://paleodb.org/cgi-bin/bridge.pl>), which collates age and locality data for more than 170,000 taxa in approximately 100,000 collections. An important feature of such a comprehensive resource is that it facilitates the normalization of sampling in ways that reduce the distorting effects of collection bias (e.g., Alroy et al., 2008; Alroy, 2010; Kiessling et al., 2010; Peters and Heim, 2010).

Can we detect detailed trends in mineralizing episodes?

The picture of globally averaged pulses of mineralization in synchronicity with stages of supercontinent assembly is, at best, a first-order approximation. As more age data of greater precision accumulate, a more nuanced view is certain to emerge. With respect to mineral evolution and the supercontinent cycle, it is likely that orogenic events lead to a sequence of mineralizing processes. Studies of many other mineral-forming elements (Co, Cr, Ni, Au, REE, As, S) now in progress, coupled with thoughtful application of statistical tests, are required to elucidate whether this trend of sequential mineralization can be confirmed.

Efforts to detect fine details in the episodicity of minerals of different elements are hindered by limited age data thus far assembled in the Mineral Evolution Database (Hazen et al., 2011). For example, the age information we have collated for 110 Be minerals come from only 122 localities. Our understanding of Be mineral evolution would be greatly enhanced by adding more of the thousands of known beryl localities. The growing Mineral Evolution Database presently incorporates ~3,000 localities and ages, representing ~1,000 distinct mineralized districts, but much greater global coverage is needed to reveal distinctive trends for varied elements.

What processes are reflected in the complex Phanerozoic temporal record of zircon and other minerals and chemical elements?

Not only is the Phanerozoic mineralogical record more complete than that of previous eons but it also appears to be more rapidly variable and nuanced in details of mineral distributions. Bradley (2011; figs. 3–10, A1–A20) illustrated secular variations for a variety of rocks and minerals over the past 550 m.y. and demonstrated significant temporal complexities. For example, he records five or more maxima in the production of ophiolites, marine evaporites, oolitic limestone, massive sulfide deposits, and halite. Similarly, zircon data of Condie and Aster (2010) suggested three significant pulses and declines in the rate of zircon formation in the past 300 Ma. The record of recent mercury mineral evolution also displays fine structure not present in earlier eons (Hazen et al., 2012), while the Phanerozoic record of clay mineral evolution displays

complexities in both the extent and ratios of clay mineral formation (Ronov et al., 1990; Hazen et al., 2013b).

Is this complexity primarily the result of a more complete and intensely sampled recent record, or are there additional factors that make the last 500 m.y. more variable in the nature and extent of mineralization? It is possible that these fine-scaled features are unique to the Phanerozoic Eon—that at least some of these relatively short term variations arose from the increased rate of evolution among multicellular organisms of the terrestrial biosphere, and thus reflect new feedbacks between the geosphere and biosphere. On the other hand, such fine structures may be present in the more ancient rock record but have not yet been resolved in formations of Proterozoic or Archean age.

Of particular interest is the role of the evolving biosphere on mineralization. Hazen et al. (2008, 2009, 2012, 2013a, b) have pointed to the possible biological roles of atmospheric oxidation, changing ocean chemistry, the rise of the terrestrial biosphere, microbially mediated redox reactions, biomineralization, burial of reduced carbon, and the evolution of complex symbiotic root systems in Earth's changing near-surface mineralogy. And on a global tectonic scale, Naeraa et al. (2012) have suggested the provocative idea that biological feedbacks may have played a role in the transition to modern-style subduction and, by extension, the supercontinent cycle.

Conclusions

A central theme of mineral evolution research has been the striking coevolution of the geosphere and biosphere. Even as minerals appear to have been essential to life's origins and evolution, so too has life been an integral facet of the origins and evolution of the geosphere, leading to the formation of perhaps two-thirds of Earth's ~5,000 known mineral species. All aspects of Earth history appear to be interwoven, and unexpected positive and negative feedbacks among minerals, life, and tectonic cycles continue to emerge (Hazen, 2012). Consequently, an integrated approach to understanding Earth history in general, and the supercontinent cycle in particular, is essential.

Bradley (2011, p. 17) concluded that "Every secular trend can have only one correct explanation, complicated though it may be." Mineral evolution demonstrates that Earth history encompasses many interconnected secular trends—numerous complex stories in four dimensions, which must be understood both individually and collectively. As these stories unfold, a clearer picture of Earth's grandest tectonic transitions will emerge.

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