Mineral Evolution: What's Next?*

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The concept of "mineral evolution," the study of Earth's changing near-surface mineralogy through time, was introduced in an article in the November 2008 issue of *American Mineralogist* (see reprint, which is the principal background reading for this presentation). The central thesis of mineral evolution is that the near-surface mineralogy of terrestrial planets and moons diversifies through time as a consequence of varied paragenetic processes, including planetary accretion and differentiation, the evolution of igneous rocks, fluid-rock interactions, and the influences of life. Mineral evolution thus seeks to frame mineralogy in an historical context by focusing on changes through time of a variety of Earth's near-surface characteristics, including mineral diversity; mineral associations; the relative abundances of mineral species; compositional ranges of their major, minor and trace elements and isotopes; and grain sizes and morphologies (Hazen et al. 2008; Hazen and Ferry 2010). Mineral evolution also exemplifies aspects of many complex evolving systems, in that we observe complexification (i.e., diversification) through time and each stage of mineral evolution depends on the sequence of prior stages (Hazen and Eldredge 2010).

This approach to mineralogy, which underscores similarities and differences in the evolution of different terrestrial planets and moons and points to the co-evolution of the geosphere and biosphere, has received significant discussion (e.g., Rosing 2008; Perkins 2008; Vasconcelos and McKenzie 2009; Johnson 2009). While much of this analysis has been favorable, mineral evolution has also been criticized, for example on the basis that its central premise is not new, that the framework lacks a useful predictive component, and that the use of the word "evolution" is inappropriate in the context of mineralogy.

Much of the subsequent effort in mineral evolution research has thus addressed these important criticisms (Hazen et al. 2009, 2011; Grew & Hazen 2009, 2010a, 2010b; *Elements* 2010). Several of these studies have focused on specific chemical elements and the first appearances of mineral species containing those elements through time (Figures 1 and 2). These studies reveal striking and as yet unexplained episodic increases in the diversity of mineral species, notably in the intervals 2.0 to 1.7 and 0.6 to 0.2 billion years ago.

Other studies correlate the relative abundances of minerals to geologic conditions (Figure 3). Special attention has also been focused on changes in clay mineralogy, both in absolute and relative terms (Kennedy et al. 2006; Elmore 2009; Tosca et al. 2010). Of note is the massive compilation of Ronov and colleagues (1990), who documented relative clay mineral abundances from approximately 10,000 dated shale samples collected across the Russian Platform – a remarkably large, yet potentially idiosyncratic data set representing the past 1.3 billion years. Sverjensky et al. (2010) demonstrate that these data, which reveal dramatic fluctuations in the relative proportions of kaolinite, chlorite, montmorillonite, and illite, correlate with estimated variations in atmospheric O_2 and CO_2, as well as with the rise of deep-rooted vascular plants after 400 Ma and the appearance of associated ectomycorrhizal fungi (symbiotic root-associated fungi with hyphae that penetrate the soil) at ~200 Ma (Taylor et al. 2009).

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*Adapted in part from Hazen et al. (2011)

A MINERAL EVOLUTION DATABASE

Advances in mineral evolution depend on the availability of detailed information on mineral localities of known ages and geologic settings. A comprehensive database including this information, employing the mindat.org website as a platform, is now being implemented. This resource will incorporate software to correlate a range of mineral occurrences and properties versus time, and it will thus facilitate studies of the changing diversity, distribution, associations, and characteristics of individual minerals as well as mineral groups. The Mineral Evolution Database thus holds the prospect of revealing mineralogical records of important geophysical, geochemical, and biological events in Earth history.

Mineral evolution studies involve correlating mineralogical variables with time and evolving geologic setting. Extensive tabulations of mineral species and localities (notably http://mindat.org) have proven critical in this effort. However, the principal impediment to advancing studies of mineral evolution is the lack of a comprehensive database that links such mineral species and locality information with ages and geologic context. Much of the necessary geochronological data exist in the literature, but in widely scattered primary sources. Consequently, documenting the age distribution of a single mineral species may require locating ages of several thousand localities in dozens of countries.

To advance this effort we have initiated development of a Mineral Evolution Database that will link to existing mineral species and locality data in the comprehensive mindat.org database. This effort is proceeding on two fronts. First, we are beginning a systematic survey of the primary literature to compile all mineral localities with known ages and their geologic settings. This massive undertaking requires the compilation of data on approximately 100,000 mineral localities. However, such database construction will only have to be done once to provide the essential foundation for future mineral evolution studies.

This large-scale effort finds is analogous to the Paleobiology Database (http://paleodb.org/cgi-bin/bridge.pl), an international, community-based project to make fossil occurrence data available to all paleontologists. To date, data have been entered for more than 170,000 taxa and nearly 100,000 collections. As discussed below, this large and growing database not only enables paleontologists to track taxa and assemblages through time (and across environments), but also to normalize sampling in ways that reduce the distorting effects of collection bias (e.g., Alroy et al., 2008; Kiessling et al., 2010; Peters and Heim 2010; Alroy 2010).

Mindat.org has been running online since October 2000 and is now the largest online database of mineralogical information. The core purpose of mindat.org is to record information about mineral localities worldwide, to list the reported and verified mineral species at these localities, and, where possible, to provide photographs of these localities and their mineral specimens. There are currently over 20,000 registered users on mindat.org, of whom several hundred active contributors submit data and photographs for the project. A management team of approximately 25 members helps to verify new submissions, and a discussion forum allows the wider community to question and validate new postings.

The mindat.org website is based on the open source PHP and MySQL systems, using custom software developed primarily by Jolyon Ralph. This software will be updated to allow age information to be entered for use in this mineral evolution project. An advantage of employing the Mindat platform is that data can be exported easily to and from other mineral databases, such as GEOROC and PetDB.

Currently the mindat.org system allows mineral occurrence information to be recorded for each known locality. This capability will be edited to allow those with appropriate access permissions to add information about the age range for each mineral species that has been dated from a particular deposit. This project will thus require those who wish to contribute data to be validated and to have an extra level of access clearance granted to their mindat.org login account. This clearance will allow them to edit and update information on mineral ages.

Special care will be required in identifying the ages of minerals, as opposed to the ages of their host formations. The richness of many mineral localities is a consequence of multiple stages of alteration, which make dating of individual phases difficult. Changes to mindat.org will thus allow managers of the site and administrators of this project to review and, if necessary, modify age information. The site will show who made the changes, what those changes were, and when they were made. All changes will include a valid bibliographic reference for the source of the data. Additions and changes will include both edits to existing mindat.org localities and the inclusion of new localities not currently in the system.

A second parallel effort is development of a software package that will permit flexible data mining of mineral occurrences versus age data. A set of search options will allow users to identify the distribution of occurrences of each mineral species through time, including the earliest and most recent occurrences. It will also be possible to bin these data according to distinctive paragenetic modes or geographical regions. The mindat.org platform is now being modified to facilitate this capability.

In addition, software will be created to allow graphical representation of these data, for example by plotting the age distribution of all localities for a given mineral species, or by plotting the ages of first appearance for all minerals in a related group (e.g., minerals of beryllium or sulfate minerals). These searches, which will become more useful over time as more locality age data are entered, will include the ability to show data in both geographical context (on a modern world map) and chronologically.

UNANSWERED QUESTIONS IN MINERAL EVOLUTION RESEARCH

Mineral evolution represents an alternative framing of mineralogy – an approach that complements more traditional presentations of the subject based on solid-state chemistry and physics. Certainly there is considerable pedagogical power in presenting mineralogy in the context of the narrative sweep of Earth history, including nebular evolution, planetary accretion and differentiation, initiation of plate tectonics and continent formation, the evolving composition of the atmosphere, the origins of life, and the evolution of varied biochemical pathways and ecological niches. But does mineral evolution offer anything new as a predictive methodology? Is there anything that might guide mineralogical research in new directions?

The key to development of mineral evolution is to examine previously unrecognized temporal trends in mineral properties and distributions by adding the time dimension to mineralogical studies. Consider the following unanswered questions, each of which presents avenues for research that would be facilitated by the proposed mineral evolution database.

1. Are there temporal trends in the first appearances and cumulative numbers of mineral species? A database with all localities and their ages for the >4500 known mineral species will enable analysis of the diversification of Earth's near-surface mineralogy through time. Studies on the first appearances of minerals of Be and B (Grew and Hazen 2009, 2010a, 2010b) and work in progress on the minerals of Hg, Mo, W, Cu, I, and Br point to possible pulses in their origins.

However, a comprehensive database of all mineral locality ages is required to distinguish statistically significant increases in the numbers of mineral species from non-uniform temporal distributions of known mineral localities.

One important opportunity is to identify mineral species that are highly sensitive to environmental conditions and, consequently, that reflect aspects of Earth's geochemical, tectonic, and biological evolution. For example, species such as cassiterite (SnO_2), pollucite [$(Cs,Na)_2Al_2Si_4O_{12}•(H_2O)$], and a number of minerals found in massive sulfide deposits (including rare sulfides and sulfosalts) may serve as indicators of highly differentiated magmatic and hydrothermal systems, or of multiple recycling of evolved continental crust. High-pressure minerals such as coesite and magnesiodumortierite are largely restricted to crustal rocks subjected to ultrahigh-pressure metamorphism during subduction. Mineral data could thus possibly provide significant constraints on early history of fluid-rock interactions, crustal and mantle dynamics, and the establishment of plate tectonics.

Another potentially revealing research topic is to track detrital minerals and the minerals included in them through time. A wealth of relatively low-grade sedimentary rocks, some as old as 3800 Ma, preserve detrital mineral suites that provide forensic data on surface lithologies subjected to erosion. In what may be seen as a precursor study, Taylor and McLennan (1985) used the elemental composition of Archean and Proterozoic shales to infer crustal history. Most previous mineralogical efforts have focused on zircon, but research could be expanded to the whole suite of detrital minerals.

Systematic surveys of the cumulative numbers of mineral species can reveal if there were pulses of mineral formation, waxing and waning of mineral-forming processes, or even episodes of "mineral extinction." As noted above, paleontological surveys of the number and distribution of fossil species, properly corrected for the areal distributions and ages of fossiliferous formations, have revealed dramatic pulses of biodiversification as well as mass extinctions (Sepkoski 1997; Alroy et al. 2008; Alroy 2010). Similar statistical treatments of mineral diversity through time hold the promise of revealing analogous patterns in Earth's mineral evolution. Note, however, that unlike the irreversible extinction of biological species, mineral species that disappear from the rock record in one formation commonly reappear elsewhere as old paragentic conditions are repeated or new paragenetic modes come into play.

An important task in this regard is to conduct a survey of the number and areal extent of mineral localities through time in order to document the absolute number or percentage of localities versus time. Any claims of mineral diversification or extinction events must be scaled to such locality/age statistics, as raw occurrence values will reflect, at least in part, the mapped availability of rocks of differing age and geologic setting. For example, geochronologic studies of zircon reveal a general lack of ages between 2.45 and 2.22 Ga, bracketing the time of three major Paleoproterozoic glacial events (Bekker et al. 2005; Condie and Aster 2009). Such gaps in the rock record must be factored into any analysis of mineral diversity through time.

2. What do changing mineral assemblages through time reveal about changes in near-surface environments? Mineral occurrences through time may provide sensitive indicators of near-surface geochemical environments, including atmospheric and oceanic chemistry, and could thus serve as monitors of pO_2 and pCO_2 through Earth history. For example, banded iron formations (BIFs) have been cited as especially sensitive indicators of Precambrian geochemistry. Their mineralogy, including relative proportions of magnetite, hematite, iron carbonates, and other phases, as well as their volumetric extents through time, show clear temporal trends that may partly reflect oxygenation of the oceans (Klein 2005; Bekker et al. 2010).

Systematic variations of carbonate minerals through time are of special interest in documenting the evolution of Earth's oceans and atmosphere. For example, the precipitation of calcite versus aragonite forms of $CaCO_3$ records secular variations in the Mg/Ca of seawater (Stanley and Hardie 1998; Hardie 2003). Strontium content is an important indicator of primary aragonite composition, even if precipitated aragonite has subsequently transformed to calcite.

Evaporite minerals reveal details of terrestrial environments as well as the composition of the stranded water bodies from which they precipitated. For example, jarosite $[(K,Na,H_3O,X^{+1})Fe^{3+}{}_3(OH)_6(SO_4)_2]$, a family of hydrous iron sulfate minerals, indicates acidity at the time of its formation. Therefore, the discovery of jarosite in >3 Ga sedimentary rocks on Mars helps to illuminate the surface history of that planet (Squyres et al., 2004). Clay minerals are also important in documenting evolution of Earth's near-surface environments (Tosca et al. 2010; Elmore 2009; Sverjensky et al. 2010), including changes in ocean and atmospheric composition, the geochemistry of near-surface aqueous fluids involved in diagenesis and low-grade metamorphism, and the rise of terrestrial biota.

Other mineral indicators might have the potential to confirm and constrain the proposed pulses of oxidation in the Neoarchean Era, to provide evidence for the emergence of new modes in continental weathering in the Paleozoic Era, or to track the oxidation state of near-surface aqueous fluids involved in rock alteration and ore formation. A first step might be to arrange mineral species and assemblages according to the minimum log fO_2 required for their formation at plausible near-surface conditions, and then relate those minima with first appearances in the geological record. For example, minerals stable at $\log pO_2 \sim -72$ (the hematite-magnetite buffer at standard temperature and pressure) are likely to have been found at or near Earth's surface since the Hadean Eon, whereas minerals containing Mo^{6+}, U^{6+}, Hg^{2+}, Cu^{2+} and Mn^{4+} likely appeared later in Earth history at times of higher pO_2. Furthermore, if distinctive lithological and textural characteristics offer hints at the depth of emplacement (e.g., the average grain size of a granite), then it might be possible to estimate temporal changes in the oxygen fugacity of near-surface fluids as a function of depth. Much of the necessary geochemical and mineralogical data to constrain models of Earth's near-surface redox history already exist, but these data need to be compiled and systematized in a chronological scheme.

Ratios of trace and minor elements and isotopes, especially of redox-sensitive elements, represent an important opportunity for further research. Temporal studies of variations of Th/U in black shales (Partin et al. 2010) and Re/Mo in molybdenite (McMillan et al. 2010) over 3 billion years of Earth history demonstrate that elemental ratios are sensitive indicators of changes in Earth's near-surface environment. Several common minerals and mineral groups, including biopyriboles (i.e., amphiboles, pyroxenes, and micas), garnet, spinel, chlorite, and tourmaline, possess crystal structures that can accommodate dozens of different chemical elements. Systematic investigation of minor and trace elements in these minerals through time could reveal trends that reflect the emergence of new modes of fluid-rock interaction, changes in ocean and atmospheric chemistry, and the influences of living systems.

Such investigations will be complicated by the multiple paragenetic modes that are responsible for many mineral species. Such variables can be minimized by focusing on one specific lithology, for example amphibole and mica from fine-grained (i.e., shallow emplacement) granites, through time.

3. What are the complete lists of minerals from given periods of Earth history and do those lists reveal distinctive environmental characteristics of those periods? As we obtain age information for a significant fraction of all known mineral localities, it would be instructive to compare the mineral diversity through the different eras of Earth history. For example, what are implications of the dozen or so known Hadean mineral species preserved as inclusions in ancient zircons, and do those minerals possess distinctive chemical or isotopic characteristics? Do minerals reflect the biological innovations of the Archean Eon's four Eras (Eoarchean, 3.85-3.6 Ga; Paleoarchean, 3.6-3.2 Ga; Mesoarchean, 3.2-2.8 Ga; and Neoarchean, 2.8-2.5 Ga) – a time when life arose and metabolic processes such as nitrogen fixation and photosynthesis evolved? Similarly, how is the rise of atmospheric oxygen in the Paleoproterozoic Era (2.5-1.6 Ga) reflected in Earth's near-surface mineral diversity? More recently, is the rise of land plants or the late Mesozoic expansion of flowering plants reflected in changing mineralogy?

A closely related opportunity lies in documenting what might be termed the "half-life" of mineral species – the average near-surface residence time for minerals in environments subject to erosion, weathering, or other destructive alteration processes. For example, some zircon crystals have survived from at least 4.4 Ga, in sharp contrast to evaporite or clay minerals, which are more easily altered, eroded, or otherwise removed from the geological record. Similarly, distinctive minerals associated with serpentinization zones of ocean basalts, or ultra-deep metamorphic zones with high-pressure minerals (e.g., jadeite and coesite), are unlikely to survive much longer than 100 Ma in the dynamic environments associated with plate tectonic processes.

Clay minerals present a particularly intriguing and challenging case of mineral survivability. Reports of clay minerals are sparse for rocks older than the Late Archean (e.g., Tosca et al. 2010). Does the paucity of older clay minerals primarily reflect their lack of durability (i.e., an inherently short mineralogical half-life) or rather was there also a significantly reduced clay mineral production prior to 2.5 Ga? Are clay minerals in older rocks original, or were they formed more recently by alteration? Why are ancient clay minerals apparently preserved so well on Mars (Ehlmann et al. 2008) compared with the terrestrial environment? In the absence of plate tectonic activity, can clay minerals survive for eons in near-surface environments?

In considering the complete inventory of minerals from a given geologic age, it is also intriguing to consider the distribution of trace and minor elements. Prior to the first minerals of Be and B, where did these elements reside? Were they present as dispersed trace elements in other phases, either in solid solution or in defects? Did they concentrate along grain boundaries, and if so in what form? Are there as yet unrecognized nano-phases? These questions are tied closely to traditional concerns of crystal chemistry and the first appearances of varied cation polyhedral and other structural motifs of the mineral kingdom.

4. For a given mineral species, what is the age distribution of all known samples; were there periods of increased or reduced rates of mineral formation? It is possible that geochemical, tectonic, or biological events may be manifested in the increased production or suppression of certain key mineral species. A comprehensive survey of all known occurrences of a species through time might thus reveal pulses or gaps. For example, a plot of the approximately 4000 known localities of molybdenite versus time, especially if coupled with trace and minor element data and correlated with paragenetic mode, might reveal details of near-surface oxygenation, bioavailability of Mo, the initiation of nitrogen fixation by the Mo-bearing nitrogenase enzyme, and other key events. Furthermore, regional variations in these data might reveal otherwise hidden aspects of paleogeography and tectonic history.

5. What can we learn from changes in crystal morphology through time? The crystal habits of minerals are influenced by environmental factors, including temperature, pressure, composition of aqueous solutions, and biological activities (Babel 1990; Cody and Cody 1991; Orme et al. 2001; Pope et al. 2000). Calcite ($CaCO_3$), for example, is known to occur in dozens of distinct crystal forms – variations that may reveal much about environmental conditions (Teng and Dove 1997; Teng et al. 1998, 2000). Many different organisms precipitate calcite or aragonite in tests and shells (e.g., Stanley and Hardie 1998; Knoll 2003), and still others facilitate or inhibit $CaCO_3$ nucleation and growth due to the chemical properties of their metabolic products or the physicochemical properties of organic exudates (Pentacost 2005). Systematic surveys of calcite crystal morphology, therefore, might reveal previously unrecognized trends in environmental conditions, including ocean chemistry, hydrothermal systems, and biological innovations.

6. Can minerals provide unambiguous biosignatures (or "abiosignatures") in our search for life on other worlds? Hazen et al. (2008) concluded that approximately two-thirds of known mineral species on Earth are the indirect consequence of biology, mostly as a consequence of the GOE. If so, then many mineral species may provide an unambiguous signature of a living world. Minerals from the oldest rocks may help to constrain which minerals were involved in the origin of life (Papineau 2010) and prove to be robust and easily detected in the search for extraterrestrial life. That said, we must be cautious, as the expanded repertoire of minerals actually reflects the availability of oxygen, not minerals synthesized solely or even principally by organisms. On Mars the presence of oxides and sulfides reflects redox conditions at and near the planetary surface, whether or not biology influenced those conditions.

Biominerals represent another important topic for further research. Which mineral species are produced exclusively by life? Similarly, are some mineral varieties, including those with distinctive compositions (e.g., Th-depleted uraninite) or morphologies (e.g., nano-uraninite), unambiguously formed by biological processes? A fuller understanding of the dependence of mineral diversity on biology is thus a key objective of mineral evolution studies.

These unanswered questions in mineral evolution outline a multi-decade program and represent great opportunities for the mineralogical community.

CONCLUSIONS

What does mineral evolution have to offer that is new? Plots of the diversity of mineral species through time are an important first step, and they may reveal pulses of mineral formation (and possible "extinction") that point to important changes in Earth's near-surface environment. For this reason, a comprehensive data base that records ages and geologic setting for all known mineral localities will allow much more varied and subtle questions to be addressed. With access to a comprehensive Mineral Evolution Database and flexible data mining procedures, numerous other questions of this kind could be posed. Thus, the Mineral Evolution Database could lead to original research studies that are difficult to undertake in any other way.

It is too soon to predict what will be found in such a systematic survey of Earth's mineralogy through time. However, we can be confident that new and as yet unsuspected mineralogical markers for such key events as the initiation of plate tectonics, the formation of continents, the origins of life, the global rise of atmospheric oxygen, the greening of the terrestrial environment, and numerous other biological innovations are awaiting discovery.

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FIGURES

Figure 1. Plot versus age of the cumulative number of known species of 107 Be minerals of 108 total (the age for jeffreyite could not be established from the available data) and 263 B minerals based on literature search (Grew and Hazen unpublished data). The plot is cumulative because each reported new appearance is added to the number of minerals having been reported prior to the age of the appearance. The plot is not meant to indicate the totality of minerals forming in the Earth's near surface at any given time, including the present; i.e., some minerals formed once or over a limited time interval, and have not formed since. (Courtesy of Edward Grew)

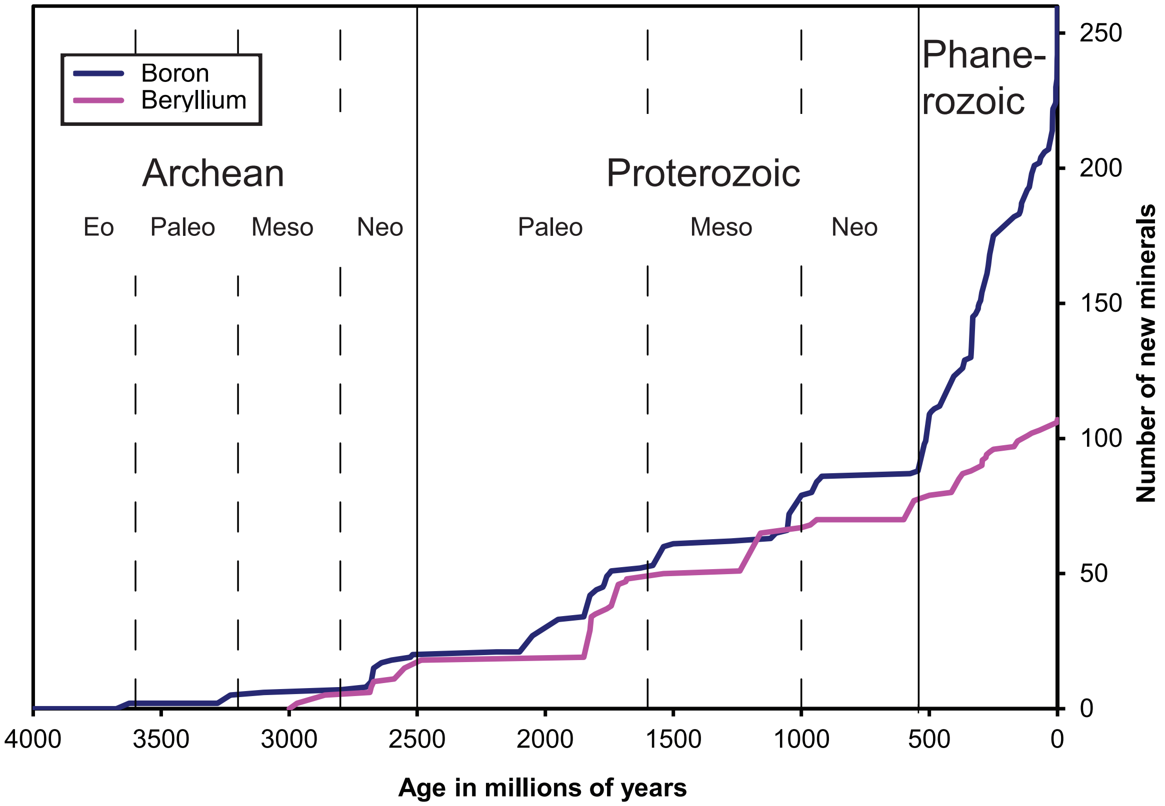

Figure 2. Preliminary plot versus age of the cumulative number of known species of Hg and Mo minerals based on literature search (Golden et al. unpublished data). The plot is cumulative because each reported new appearance is added to the number of minerals having been reported prior to the age of the appearance. Compare the apparent pulses of new mineral formation at c. 2.0 to 1.7 and 0.6 to 0.2 Ga with data for Be and B minerals in Figure 1 (Courtesy of Joshua Golden)

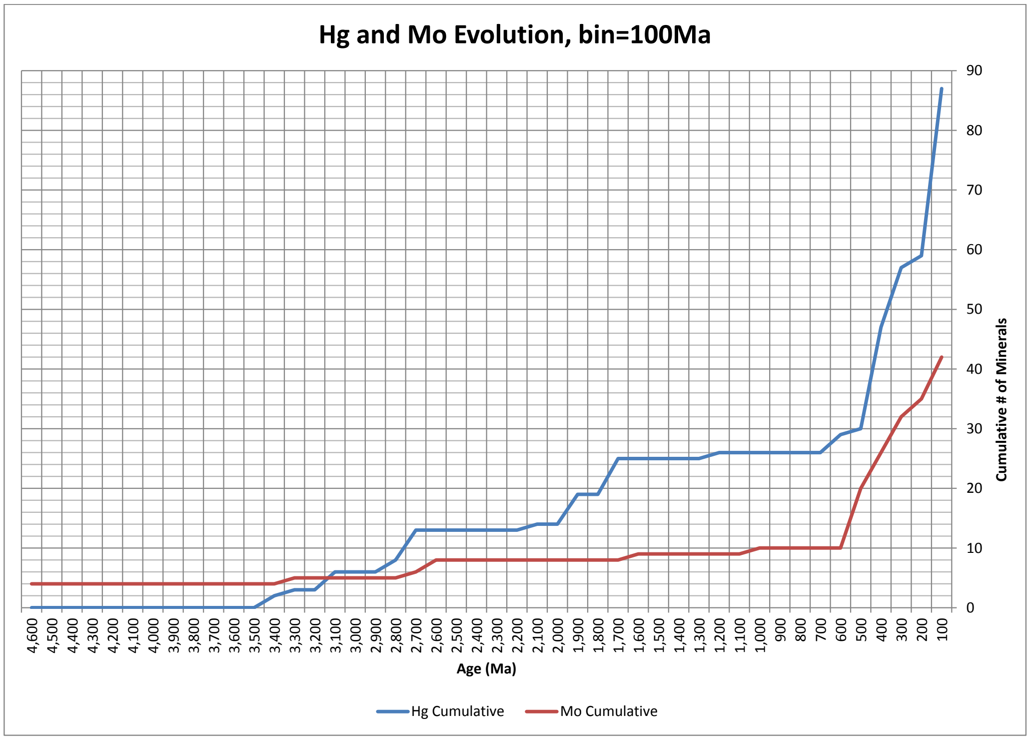

Figure 3. Ronov et al. (1990) documented relative clay mineral abundances from approximately 10,000 shale samples collected across the Russian Platform, representing the past 1.3 billion years. Sverjensky et al. (2010) noted that fluctuations in relative clay abundances over the past 600 million years correlate with variations in atmospheric O_2 and CO_2. For example, the relative abundance of chlorite in shales tracks values of the level of atmospheric O_2 inferred from the GEOCARBSULF model (Berner 2006). (Red labels represent abbreviations for geological time intervals.) The deviations from this correlation in the past 200 million years might reflect the rise of mycorrhizal fungi. (Courtesy of Dimitri Sverjensky)