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(Article begins on next page)

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Needs and opportunities in mineral evolution research

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ABSTRACT

Progress in understanding mineral evolution, Earth's changing near-surface mineralogy through time, depends 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.

Keywords: philosophy of mineralogy, database, isotope geochemistry, origins of life, mineral data

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INTRODUCTION

"Mineral evolution" 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). This approach to mineralogy, which underscores similarities and differences in the evolution of 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). However, the framework for a program of research that aims to achieve a systematic survey of Earth's mineralogical history is thus far lacking. Here, our three objectives are (1) to review recent examples of diverse efforts in mineral evolution research; (2) to describe the development of a comprehensive Mineral Evolution Database that ties ages and geologic settings to minerals from numerous localities; and (3) to pose a range of unanswered questions related to Earth's changing near-surface mineralogy that could be addressed by employing such a database.

EXAMPLES OF MINERAL EVOLUTION RESEARCH

Many authors have already presented data on the temporal variation of individual or collective mineral properties without invoking the term "mineral evolution." Although motivated by different questions, and implemented using varied types of geochemical and mineralogical data, these studies exemplify both the promises and challenges of mineral evolution research.

Isotope Compositions

Geochemists have long recognized the importance of changing isotope ratios through time as records of major geophysical, geochemical, and biological events in Earth history. In the case of sulfur isotopes, changes in the range of $\delta^{34}S$ values with time have been linked to the evolution in the concentration of sulfate in the oceans and changes in the relative amounts of sedimentary pyrite formation in the marine environment and weathering on the continents (Monster et al. 1979; Canfield et al. 2000; Habicht et al. 2002; Berner 2006; Schroeder et al. 2008). Temporal changes in the range of $\Delta^{33}S$ ($\approx \delta^{33}S - 0.515\delta^{34}S$) have been tied to changes in atmospheric composition, specifically to the time when the accumulation of oxygen in the Paleoproterozoic atmosphere eventually led to conditions in which the production and preservation of mass-independent fractionations (MIF) of sulfur isotopes by photochemical reactions were inhibited (Farquhar et al. 2000, 2001; Pavlov and Kasting 2002; Bekker et al. 2004; Papineau et al. 2005, 2007; Ono et al. 2006, 2009; Domagal-Goldman et al. 2009; Guo et al. 2009; Hofmann et al. 2009; Halevey et al. 2010). Small sulfur isotope MIF are also used to track changes in the ecology of sulfur-metabolizing organisms in Earth's oceans since the rise of atmospheric oxygen (Johnston et al. 2005; Wu et al. 2010). Figure 1, which illustrates the present state of knowledge of the $\Delta^{33}S$ record versus time, reveals both the dramatic decrease in the variability of $\Delta^{33}S$ after

~2.4 Ga and the smaller-scale variability that is preserved by sulfate minerals and sulfate trapped in carbonate minerals for the more recent part of the geologic record. The convergence of Δ^{33}S to values within a few tenths of a permil of zero, combined with an expansion in the range of variability for δ^{34}S, is interpreted to reflect changes in sulfur chemistry associated with the rise of atmospheric oxygen, the development of a UV-protecting ozone layer, and the onset of significant amounts of oxidative weathering. These observations also corroborate other mineralogical observations that suggest a contemporaneous rise in atmospheric oxygen, the "Great Oxidation Event" (GOE). The presence of anomalous Δ^{33}S in sulfide inclusions in diamond has also been interpreted as evidence for the plate tectonic cycling of sulfur from Earth's atmosphere into the mantle as early as ~3 Ga and then its return to the surface (Farquhar et al. 2002; Thomassot et al. 2009). A goal for future sulfur isotope research will be to correlate geochemical observations with the formation of the specific minerals that preserve these isotopic records and to understand the details of how the MIF signals are transferred from the atmosphere, to the oceans and biosphere, and ultimately to their preservation in the rock record.

The mineral zircon ($ZrSiO_4$) is especially useful in mineral evolution studies because zircon is a relatively common mineral in coarse-grained siliciclastic rocks, individual zircon grains persist in the rock cycle, it is relatively easy to date individual uranium-bearing zircon grains, and zircon's isotopic and trace element compositions are sensitive to conditions of formation (Ireland and Williams 2003; Valley 2003; Hoskin and Schalteggar 2003; Cavosie et al. 2007; Trail et al. 2007). Accordingly, Valley and coworkers (Valley et al. 2005) analyzed oxygen isotopic compositions of igneous zircon grains from 1,200 rocks spanning more than 96% of Earth history (Figure 2). They found that varying δ^{18}O values point to the emergence of crust recycling, crust-mantle interactions, and extensive oxygen isotope exchange between minerals and the hydrosphere. The zircon data show that oxygen isotope ratios of magmas were generally closer to the average mantle value of 5.3 ± 0.6 ‰ throughout the first two billion years of Earth history, though with significant positive deviations of up to 2 ‰ that point to the variable involvement of an early hydrosphere. After 2.5 Ga, higher $\delta^{18}O$ values document incorporation of increasing amounts of high-$\delta^{18}O$ supracrustal material into granitic magmas. These variations indirectly record the processes of surface erosion, sedimentation, and diagenesis that involved isotopic exchange of minerals with water at relatively low temperature. The largest reservoir of high-$\delta^{18}O$ rocks would have been clay-rich (mature) shales and mudstones, which became more abundant after 2.5 Ga owing to the development of large, stable landmasses and more intense chemical weathering after the rise of atmospheric oxygen, when CO_2 became a dominant greenhouse gas in the atmosphere and groundwaters became more acidic due to oxidation of sulfides on the continents (Bekker and Kaufman, 2007; Holland, 2002). Thus the evolution of clay minerals, responding to changes such as the GOE and the expansion of cratons and, therefore, epeiric seas, has affected the composition of magmas and the zircons they contain (Valley et al. 2005). Oxygen isotopes in zircons have the potential to document the end of the Hadean "steam atmosphere" on Earth (~4.3 Ga) and the beginning of the era when more clement conditions became available for the emergence of life (Sleep et al. 2001; Valley et al. 2002, Valley 2008).

Chemical Compositions

The major, minor, and trace element compositions of minerals can provide sensitive indicators of environmental factors at the time of their formation. For example, Nash et al. (1981) and Hazen et al. (2009) catalog several distinct modes of formation of uraninite (UO_2).

Uraninite with a significant thorianite (ThO_2) component, which is typical for the late-stage felsic melt segregations such as pegmatites, was stable in an anoxic atmosphere and concentrated in Archean placer deposits. After the rise of atmospheric oxygen, uranium (but not thorium) became soluble in oxidized solutions and precipitated as low Th/U uraninite at redox boundaries, such as contacts with rocks with high concentrations of biologically derived reducing organic compounds.

Isotopic and element compositions and elemental ratios in black shales have received special attention because they preserve information about both the nature of terrestrial erosion and deepwater depositional environments (e.g., Anbar et al. 2007; Rouxel et al. 2005; Scott et al. 2008, 2011; Partin et al. 2010). These studies, with the exception of that by Rouxel et al. (2005), have focused primarily on bulk shale properties rather than those of specific micro-mineral phases; nevertheless, temporal variations in mineral composition and other characteristics lie at the heart of this effort. Thus, for example, secular changes in the iron chemistry of carbonaceous shales has helped to establish long-term redox states of deep water in the world's oceans. In particular, unusual enrichments in Fe provide evidence for expanded anoxia in the oxygen-minimum zones of Proterozoic oceans, while the enhancement of siderite instead of pyrite deposition at about 800 Ma points to a decline in the extent of euxinic conditions significantly before the deep ocean became oxygenated (Canfield et al. 2008; Lyons et al. 2009; Johnston et al., 2010).

Partin et al. (2010) document both U concentration and Th/U ratios in black shales over 3.5 billion years of Earth history. They describe a significant increase in U content in carbonaceous shales (possibly as nano-precipitates of uraninite and U^{4+}-silicates) shortly after the rise of atmospheric oxygen at ca. 2.32 Ga (Bekker et al. 2004). This change was associated with the mobilization of U^{6+}, which is easily transported in oxidized aqueous complexes, as opposed to Th, which occurs only in the insoluble 4+ valence state. Another study, using Mo content in organic-rich sulfidic shales as a proxy for ocean redox state (Scott et al. 2008), found that Mo content in shales increased at ca. 2.15 Ga, and again, more strongly during the Ediacaran Period (ca. 580 Ma).

McMillan et al. (2010) have described a possibly related trend in mineral chemistry in a study of several dozen molybdenite (MoS_2) specimens spanning approximately the past 3 billion years. They find that molybdenite with relatively high Re and W formed primarily during the past 1 billion years – a change perhaps related to the gradually increasing mobility of oxidized Re^{7+} and W^{6+} (compared with Re^{4+} and W^{4+}) in near-surface oxygenated waters after the GOE.

Mineral Diversity

Studies of Earth's increasing mineral diversity through time point to the occurrence of new paragenetic modes, including those related to new tectonic and biological mechanisms. Grew and Hazen (2009, 2010a, 2010b) and Grew et al. (2011) reviewed the distribution through time of the minerals of beryllium and boron (Figure 3), two quintessential lithophile elements with average crustal abundances of 2.1 and 17 ppm, respectively (Rudnick and Gao 2004). The 108 approved mineral species containing essential beryllium include 66 silicates, 28 phosphates and arsenates, 9 oxides and hydroxides, 4 borates, and one carbonate. Beryllium minerals are found most abundantly and in greatest diversity in granitic pegmatites, alkaline and peralkaline pegmatites, hydrothermal deposits associated with volcanic and shallow-level plutonic rocks, and skarns, whereas non-metasomatic metamorphic occurrences are minor and sedimentary occurrences unknown except for placers. Beryllium is a trace element, and therefore minerals containing essential Be appear only after extensive differentiation, which explains the relatively late first appearance of Be minerals in the geologic record. Based on reported finds, the oldest Be minerals are Mesoarchean, when two species formed at the Gravelotte emerald deposit in 2969 ± 17 Ma granitic pegmatites associated with a greenstone belt in South Africa (Poujol 2001). Ten more species are found in later Meso- and Neoarchean (2860 to 2550 Ma) granitic pegmatites and granulite-facies rocks of the Pilbara and Yilgarn cratons, Australia, and the Bird River Province, Canada. Two species in peralkaline rocks and a metamorphic occurrence on the Yilgarn craton bring the total of Archean Be minerals to 15. Anatectic pegmatites in the ultrahigh-temperature Napier complex, Antarctica, introduce three more species in the earliest Paleoproterozoic, the last to appear before a burst of 28 new species towards the close of the Paleoproterozoic (~1850-1715 Ma) in both pegmatites (e.g., Norrö, Sweden; Tysfjord, Norway; Tiptop, South Dakota; Red Ace, Wisconsin) and complex skarn deposits of the Långban type in Sweden. From about 1700 Ma to <1 Ma, the number of new Be minerals increased relatively steadily, with a pulse of 14 new species at 1160 Ma (Ilímaussaq peralkaline complex, Greenland). All of the "principal" episodes of Be mineralization cited by Barton and Young (2002) occurred after 1600 Ma. Barton and Young (2002) cautioned that most Be deposits are concentrated at shallow levels in the Earth's crust, and thus older occurrences could have been lost to erosion. Conversely, there are some minerals that formed only once or a few times in the course of Earth's history and have not been reported from other areas, e.g., joesmithite and harstigite from the Långban-type deposits in Sweden.

The 241 valid and 22 prospective mineral species containing essential boron include one nitride, four fluorides, and 258 oxygen compounds (borates) of which 129 contain only $B\Phi_3$ triangles and/or $B\Phi_4$ tetrahedra, where Φ = O, OH, and 129 contain additional oxyanionic complexes of Be, C, Si, P, S, or As. Volcanic and sedimentary processes, together with regional metamorphism and overall greater crustal abundance, concentrated boron sufficiently for B minerals to appear earlier in the geologic record than beryllium minerals. The tourmaline species dravite and schorl from the Isua greenstone belt, Greenland (3800 Ma) are the oldest B minerals reported, but earlier formation of B minerals, including evaporitic phases, cannot be excluded, an issue having implications for stabilization of prebiotic organic compounds (Grew et al. 2011). The next oldest minerals to be reported are bonaccordite and two more tourmalines (foitite and magnesio-foitite) in the Barberton greenstone belt, South Africa (3230 Ma) and a Cr-tourmaline in the Singhbhum craton, India (3100 Ma). Highly differentiated 2520-2670 Ma granitic pegmatites and their exocontacts, 2680-2700 Ma hydrothermal activity associated with gold deposits, and ca. 2800 Ma metamorphic rocks of Fiskenæsset, Greenland brought the total to 20 species in the Archean. The borate deposits in Liaoning and Jilin provinces, China with ca. 2050 Ma metamorphism; Mn skarns in the ca. 1825 Ma Långban-type deposits, Sweden; ca. 1950 Ma skarns in the Tayozhnoye deposit, Russia; and ca. 2000 Ma granitic pegmatites and granulite-facies metamorphic rocks of the Magondi belt, Zimbabwe contributed 32 new species in the late Paleoproterozoic, whereas Mn deposits and Mg skarns were largest contributors to 36 more species in the remainder of the Proterozoic. However, the most species, 175, are reported to first appear in the Phanerozoic, including 37 species in Mg skarns and 20 in alkaline rocks. Evaporites, fumaroles, and secondary minerals in extreme desert environments contributed another 82 species. However, these ephemeral B minerals could have also formed much earlier and, with rare exception, failed to survive later geologic events (Grew et al. 2011). The only borate reported from a Precambrian evaporite is chambersite ($Mn_3B_7O_{13}Cl$) associated with algal dolostone in the 1500 Ma Gaoyuzhuang Formation, China (Fan et al. 1999; Shi et al. 2008).

However, B isotopes are consistent with an evaporitic precursor to 2400-2100 Ma metamorphic borates in the Liaoning and Jilin provinces, China (e.g., Peng and Palmer 2002). Relict casts and B isotopes are cited as evidence for an evaporite precursor to the Paleoarchean Barberton tourmaline-rich rocks (Byerly and Palmer 1991), implying a much greater diversity of borate minerals as early as 3400 Ma.

We conclude that the geologic record provides an incomplete picture of B mineral evolution, much less so than for Be mineral evolution. As in the case of Be minerals, some B minerals are reported from only one or just a few localities; others, notably evaporitic borates, likely were removed from the geological record through erosion and alteration processes. Nonetheless, despite these caveats, we suggest that the overall increasing diversity of both Be and B minerals, together with increasing compositional diversity of solid solutions as exemplified by tourmaline-group minerals, could have resulted from increasing diversity in geologic environments and from mixing of geologic materials as Earth's crust was recycled by tectonic processes. However, uncertainties regarding the distribution and survivability of mineral species underscore the need for normalized data sets capable of distinguishing between increasing mineral diversity through time and decreasing geological loss towards the present.

Relative Abundances of Minerals

Changes with time in the relative abundances of minerals are of prime importance in understanding the evolution of Earth's near-surface environments. Economic geologists have long approached the study of ore deposits by considering the evolution of distinctive mineral associations and classes of mineral deposits (e.g., Nash et al. 1981; Bekker et al. 2010; Farquhar et al. 2010; Goldfarb et al. 2010; Leach et al. 2010).

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 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; see Figure 4).

Taken together, these investigations of changing mineral characteristics through time – isotope and elemental ratios, species diversity and distribution, associated minerals, and relative abundances – are compelling arguments that far-reaching discoveries can emerge from such an approach. However, a significant impediment to such contributions is the lack of a comprehensive database that provides age information for mineral localities.

A MINERAL EVOLUTION DATABASE

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.

Database Development

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 an illustrative analog in 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 (http://georoc.mpch-mainz.gwdg.de/georoc) and PetDB (http://www.petdb.org).

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.

Data Mining Software Development

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 way to frame 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 a long-range mineral evolution program is to examine previously unrecognized temporal trends in mineral properties and distributions by adding the time dimension to mineralogical studies. Here we explore several promising 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, spodumene ($LiAlSi_2O_6$) occurs in the 3040 Ma New Consort pegmatites in the Barberton greenstone belt, South Africa (Harris and Robb 1995); these are the oldest known differentiated pegmatites and thus point to early stages of element concentration through partial melting, crystallization, and fluid-rock interactions. Other species such as cassiterite (SnO_2), pollucite [$(Cs,Na)_2Al_2Si_4O_{12}\bullet(H_2O)$], and a number of minerals found in massive sulfide deposits (including rare sulfides and sulfosalts) may also 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. For example, Meng (1988) and Meng and Dymek (1987) reported that some metamorphic tourmalines in the 3800 Ma Isua greenstone belt, Greenland have cores inferred to be of detrital origin with compositions plotting in the fields of both metasedimentary and igneous tourmaline (Henry and Guidotti 1985), suggesting the intriguing possibility of tourmaline-bearing continental crust older than the Isua belt. Detrital almandine garnet and kyanite may also reflect Al-rich lithologies indicative of crustal reworking. Muscovite inclusions in Hadean zircon from Jack Hills, Western Australia are interpreted to suggest that magmas hosting the zircon were derived dominantly from anatexis of metasedimentary rocks, i.e., rocks with precursors deposited in a Hadean ocean (Harrison 2009). The preservation of unaltered detrital pyrite, siderite, and uraninite in Mesoarchean fluvial conglomerates has been cited as evidence for an anoxic surface environment in the Archean (Grandstaff 1980; Rasmussen and Buick 1999; Frimmel 2005; Sverjensky and Lee 2010). Studies that compare the first appearance of mineral phases on different cratons represent yet another opportunity to understand Earth's dynamic history.

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; Bambach et al. 2004; 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 may help 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. 2009; 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 can prove to be sensitive indicators of changes in Earth's near-surface environment related to geochemical and biochemical evolution. The isotopic compositions of Fe and Mo in sedimentary rocks also provide tools for reconstructing the redox history of seawater (e.g., Rouxel et al. 2005; Anbar and Rouxel 2007; Dahl et al. 2010). 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), at least 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, which could be pursued for example through the nanoscale study of chondrites, 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 can be strongly 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 have proven to be an important first step, as they appear to reveal pulses of mineral formation (and possible "extinction") that point to important changes in Earth's near-surface environment. However, 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. For example, the significance of mass-independent S isotope effects was only realized after several dozens of S isotope analyses were plotted versus time (Farquhar et al. 2000), whereas the observation of subtleties in the zircon δ^{18}O record required more than 1000 data points (Valley et al. 2005). 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 AND CAPTIONS

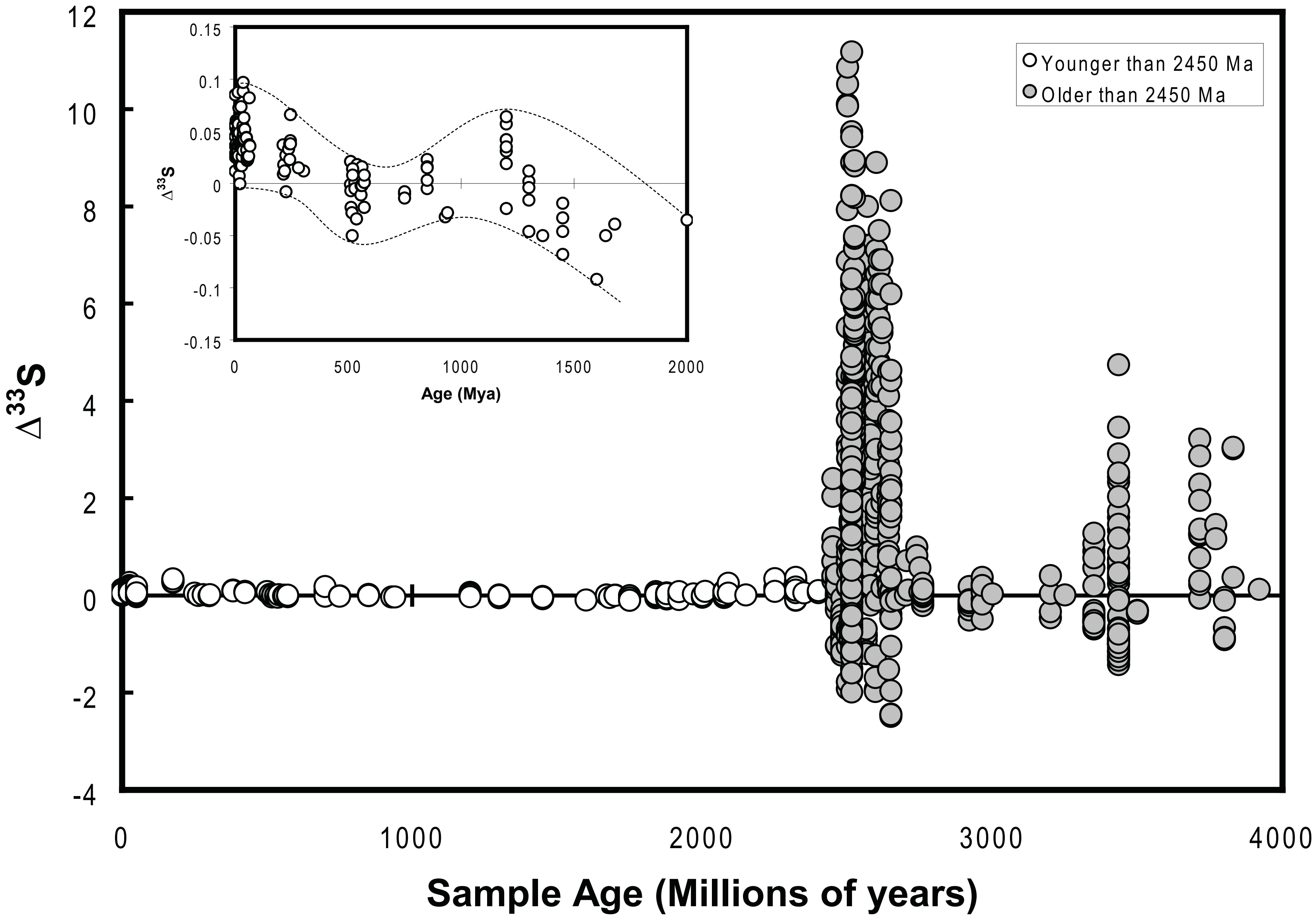
Figure 1. Plot of Δ^{33}S values versus age for sulfide and sulfate minerals. Inset shows Δ^{33}S values versus sample age for evaporite minerals and carbonate-associated sulfate. The disappearance of significant mass independent sulfur isotope fractionation in the past 2.4 billion years has been linked to the rise of a UV-shielding ozone layer during the Great Oxidation Event, and the variation in the Δ^{33}S of oceanic sulfate (inset) is interpreted to reflect changes in the microbial ecology of the oceanic sulfur cycle (data sources include Farquhar et al. 2000, 2002, 2007; Hu et al. 2003; Ono et al. 2006, 2009; Mojzsis et al. 2003; Bekker et al. 2004, 2009; Johnston et al. 2005, 2006, 2008; Whitehouse et al. 2005; Ohmoto et al. 2006; Papineau and Mojzsis 2006; Cates and Mojzsis 2006; Papineau et al. 2005, 2007; Bao et al. 2007; Philippot et al. 2007; Kaufman et al. 2007; Kamber and Whitehouse 2007; Ueno et al. 2008; Partridge et al. 2008). (Courtesy of James Farquhar)

Figure 2. δ^{18}O values of zircon grains from 1,200 rocks spanning more than 96% of Earth history (Valley et al. 2005) reveal variations in δ^{18}O values that point to the evolution of both crustal recycling and crust-mantle interactions through time. (Courtesy of John Valley.)

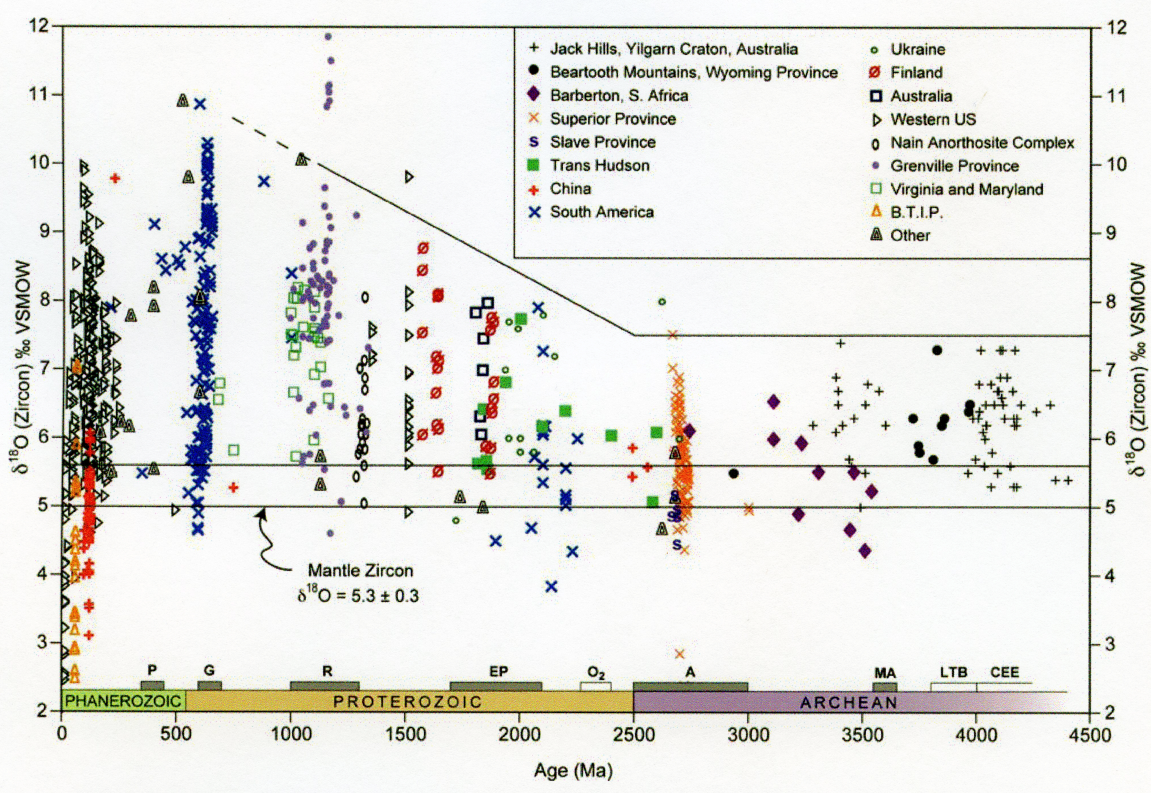
Figure 3. Plot of the reported oldest occurrences of 107 Be minerals of 108 total (the age for jeffreyite could not be established from the available data) and 263 B minerals based on literature search (Grew and Hazen unpublished data). The plot is cumulative because each reported new appearance is added 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

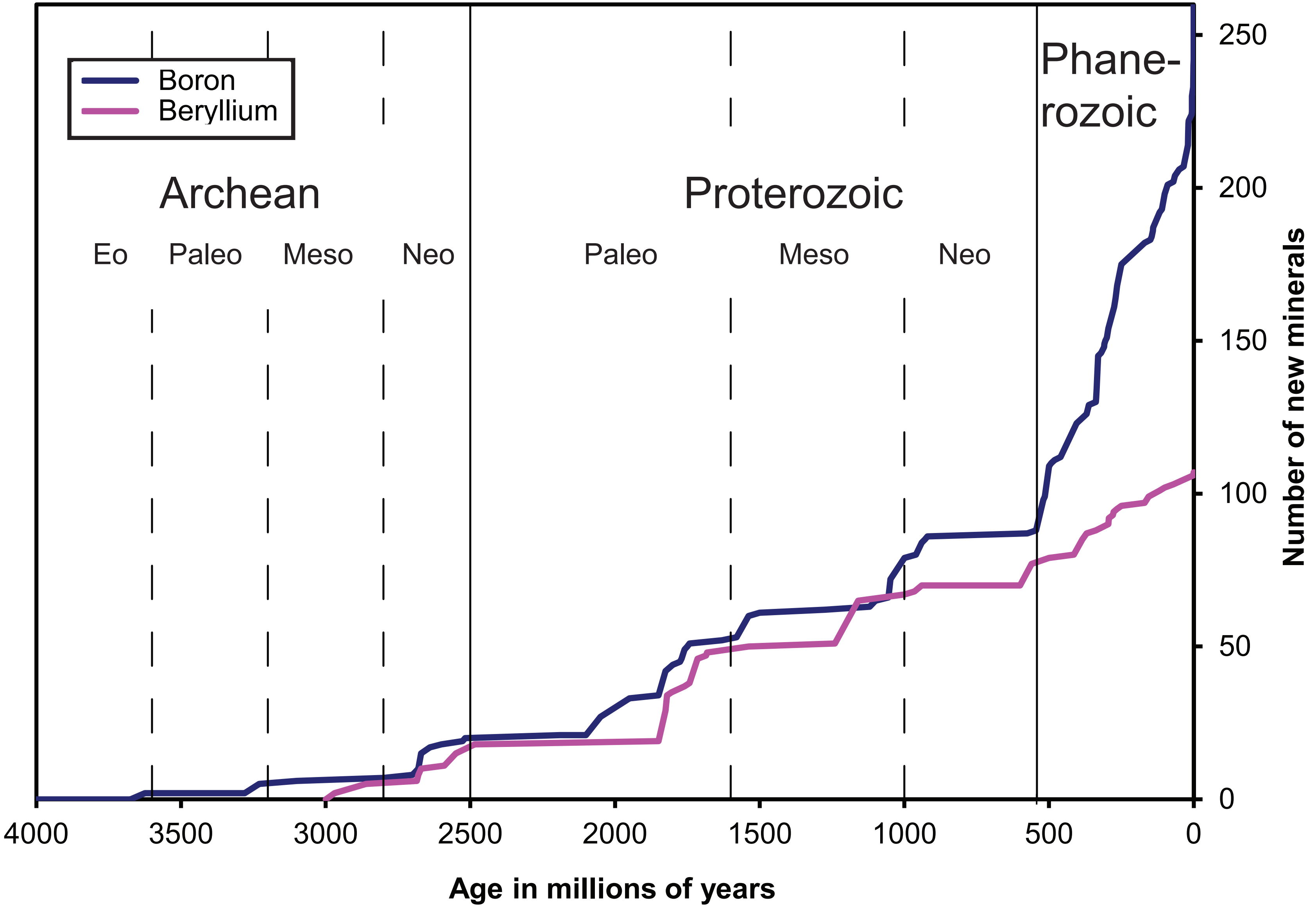
Earth's near surface at any given time, including the present; i.e., some minerals formed once or over a limited time interval, and have not formed since. (Courtesy of Edward Grew)

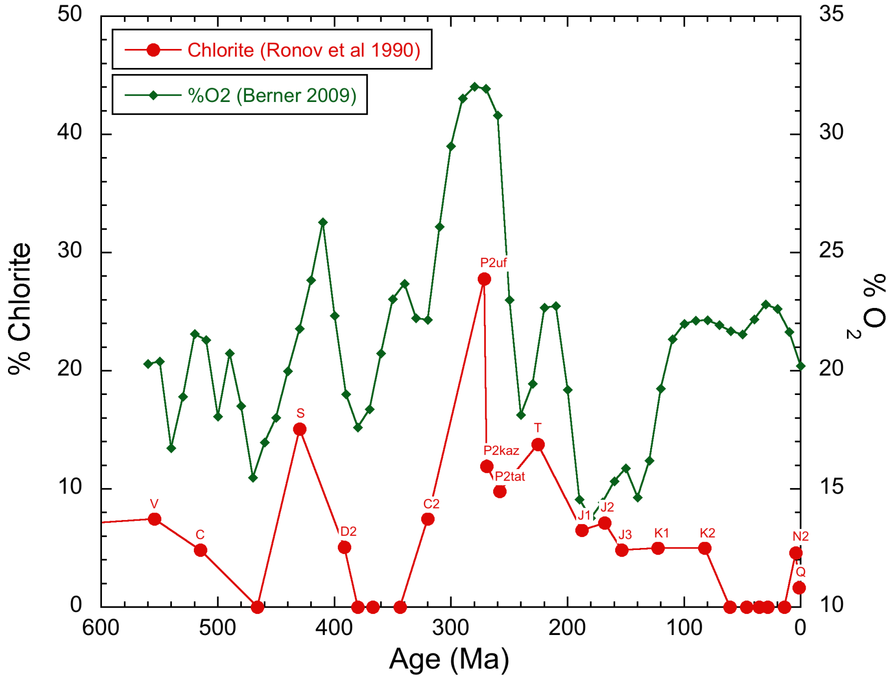
Figure 4. Ronov et al. (1990) documented relative clay mineral abundances from approximately 10,000 shale samples collected across the Russian Platform, representing the past 1.3 billion years. Sverjensky et al. (2010) noted that fluctuations in relative clay abundances over the past 600 million years 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. (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)



(Farquhar et al., 2000, 2002, 2007 Hu et al., 2003 Ono et al., 2003, 2006, 2009ab, Mojzsis et al., 2003, Bekker et al., 2004, Johnston et al., 2005, 2006, 2008


δ18O (Zircon) ‰ VSMOW
Age (Ma)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
2
3
4
5
6
7
8
9
10
11
12
Jack Hills, Yilgarn Craton, Australia
Beartooth Mountains, Wyoming Province
Barberton, S. Africa
Superior Province
Slave Province
Trans Hudson
China
South America
Ukraine
Finland
Australia
Western US
Nain Anorthosite Complex
Grenville Province
Virginia and Maryland
B.T.I.P.
Other
Mantle Zircon
δ18O = 5.3 ± 0.3
P
G
R
EP
O2
A
MA
LTB
CEE
PHANEROZOIC
PROTEROZOIC
ARCHEAN


Boron
Beryllium
Archean
Proterozoic
Phane-
rozoic
Eo
Paleo
Meso
Neo
Paleo
Meso
Neo
4000
3500
3000
2500
2000
1500
1000
500
0
Age in millions of years
0
50
100
150
200
250
Number of new minerals


Chlorite (Ronov et al 1990)
%O2 (Berner 2009)
% Chlorite
% O$_2$
Age (Ma)
50
40
30
20
10
0
35
30
25
20
15
10
600
500
400
300
200
100
0
V
C
S
D2
C2
P2uf
P2kaz
P2tat
T
J1
J2
J3
K1
K2
N2
Q