



Needs and opportunities in mineral evolution research

Citation

Hazen, R. M., A. Bekker, D. L. Bish, W. Bleeker, R. T. Downs, J. Farquhar, J. M. Ferry, et al. 2011. "Needs and Opportunities in Mineral Evolution Research." *American Mineralogist* 96, no. 7: 953–963.

Published Version

doi:10.2138/am.2011.3725

Permanent link

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1 REVISION #1 – February 2, 2011*

2 **Needs and opportunities in mineral evolution research**

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*Submitted to *American Mineralogist*, October 16, 2010.

ABSTRACT

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27 Progress in understanding mineral evolution, Earth's changing near-surface mineralogy through
28 time, depends on the availability of detailed information on mineral localities of known ages and
29 geologic settings. A comprehensive database including this information, employing the
30 mindat.org website as a platform, is now being implemented. This resource will incorporate
31 software to correlate a range of mineral occurrences and properties versus time, and it will thus
32 facilitate studies of the changing diversity, distribution, associations, and characteristics of
33 individual minerals as well as mineral groups. The Mineral Evolution Database thus holds the
34 prospect of revealing mineralogical records of important geophysical, geochemical, and
35 biological events in Earth history.

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

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INTRODUCTION

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“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

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

67 68 **Isotope Compositions**

69 Geochemists have long recognized the importance of changing isotope ratios through time as
70 records of major geophysical, geochemical, and biological events in Earth history. In the case of
71 sulfur isotopes, changes in the range of $\delta^{34}\text{S}$ values with time have been linked to the evolution
72 in the concentration of sulfate in the oceans and changes in the relative amounts of sedimentary
73 pyrite formation in the marine environment and weathering on the continents (Monster et al.
74 1979; Canfield et al. 2000; Habicht et al. 2002; Berner 2006; Schroeder et al. 2008). Temporal
75 changes in the range of $\Delta^{33}\text{S}$ ($\approx \delta^{33}\text{S} - 0.515\delta^{34}\text{S}$) have been tied to changes in atmospheric
76 composition, specifically to the time when the accumulation of oxygen in the Paleoproterozoic
77 atmosphere eventually led to conditions in which the production and preservation of mass-
78 independent fractionations (MIF) of sulfur isotopes by photochemical reactions were inhibited
79 (Farquhar et al. 2000, 2001; Pavlov and Kasting 2002; Bekker et al. 2004; Papineau et al. 2005,
80 2007; Ono et al. 2006, 2009; Domagal-Goldman et al. 2009; Guo et al. 2009; Hofmann et al.
81 2009; Halevey et al. 2010). Small sulfur isotope MIF are also used to track changes in the
82 ecology of sulfur-metabolizing organisms in Earth’s oceans since the rise of atmospheric oxygen
83 (Johnston et al. 2005; Wu et al. 2010). Figure 1, which illustrates the present state of knowledge
84 of the $\Delta^{33}\text{S}$ record versus time, reveals both the dramatic decrease in the variability of $\Delta^{33}\text{S}$ after

85 ~2.4 Ga and the smaller-scale variability that is preserved by sulfate minerals and sulfate trapped
86 in carbonate minerals for the more recent part of the geologic record. The convergence of $\Delta^{33}\text{S}$ to
87 values within a few tenths of a permil of zero, combined with an expansion in the range of
88 variability for $\delta^{34}\text{S}$, is interpreted to reflect changes in sulfur chemistry associated with the rise of
89 atmospheric oxygen, the development of a UV-protecting ozone layer, and the onset of
90 significant amounts of oxidative weathering. These observations also corroborate other
91 mineralogical observations that suggest a contemporaneous rise in atmospheric oxygen, the
92 “Great Oxidation Event” (GOE). The presence of anomalous $\Delta^{33}\text{S}$ in sulfide inclusions in
93 diamond has also been interpreted as evidence for the plate tectonic cycling of sulfur from
94 Earth’s atmosphere into the mantle as early as ~3 Ga and then its return to the surface (Farquhar
95 et al. 2002; Thomassot et al. 2009). A goal for future sulfur isotope research will be to correlate
96 geochemical observations with the formation of the specific minerals that preserve these isotopic
97 records and to understand the details of how the MIF signals are transferred from the
98 atmosphere, to the oceans and biosphere, and ultimately to their preservation in the rock record.

99 The mineral zircon (ZrSiO_4) is especially useful in mineral evolution studies because zircon is
100 a relatively common mineral in coarse-grained siliciclastic rocks, individual zircon grains persist
101 in the rock cycle, it is relatively easy to date individual uranium-bearing zircon grains, and
102 zircon’s isotopic and trace element compositions are sensitive to conditions of formation (Ireland
103 and Williams 2003; Valley 2003; Hoskin and Schaltegger 2003; Cavosie et al. 2007; Trail et al.
104 2007). Accordingly, Valley and coworkers (Valley et al. 2005) analyzed oxygen isotopic
105 compositions of igneous zircon grains from 1,200 rocks spanning more than 96% of Earth
106 history (Figure 2). They found that varying $\delta^{18}\text{O}$ values point to the emergence of crust
107 recycling, crust-mantle interactions, and extensive oxygen isotope exchange between minerals

108 and the hydrosphere. The zircon data show that oxygen isotope ratios of magmas were generally
109 closer to the average mantle value of 5.3 ± 0.6 ‰ throughout the first two billion years of Earth
110 history, though with significant positive deviations of up to 2 ‰ that point to the variable
111 involvement of an early hydrosphere. After 2.5 Ga, higher $\delta^{18}\text{O}$ values document incorporation
112 of increasing amounts of high- $\delta^{18}\text{O}$ supracrustal material into granitic magmas. These variations
113 indirectly record the processes of surface erosion, sedimentation, and diagenesis that involved
114 isotopic exchange of minerals with water at relatively low temperature. The largest reservoir of
115 high- $\delta^{18}\text{O}$ rocks would have been clay-rich (mature) shales and mudstones, which became more
116 abundant after 2.5 Ga owing to the development of large, stable landmasses and more intense
117 chemical weathering after the rise of atmospheric oxygen, when CO_2 became a dominant
118 greenhouse gas in the atmosphere and groundwaters became more acidic due to oxidation of
119 sulfides on the continents (Bekker and Kaufman, 2007; Holland, 2002). Thus the evolution of
120 clay minerals, responding to changes such as the GOE and the expansion of cratons and,
121 therefore, epeiric seas, has affected the composition of magmas and the zircons they contain
122 (Valley et al. 2005). Oxygen isotopes in zircons have the potential to document the end of the
123 Hadean “steam atmosphere” on Earth (~4.3 Ga) and the beginning of the era when more clement
124 conditions became available for the emergence of life (Sleep et al. 2001; Valley et al. 2002,
125 Valley 2008).

126

127 **Chemical Compositions**

128 The major, minor, and trace element compositions of minerals can provide sensitive
129 indicators of environmental factors at the time of their formation. For example, Nash et al.
130 (1981) and Hazen et al. (2009) catalog several distinct modes of formation of uraninite (UO_2).

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

137 Isotopic and element compositions and elemental ratios in black shales have received special
138 attention because they preserve information about both the nature of terrestrial erosion and
139 deepwater depositional environments (e.g., Anbar et al. 2007; Rouxel et al. 2005; Scott et al.
140 2008, 2011; Partin et al. 2010). These studies, with the exception of that by Rouxel et al. (2005),
141 have focused primarily on bulk shale properties rather than those of specific micro-mineral
142 phases; nevertheless, temporal variations in mineral composition and other characteristics lie at
143 the heart of this effort. Thus, for example, secular changes in the iron chemistry of carbonaceous
144 shales has helped to establish long-term redox states of deep water in the world's oceans. In
145 particular, unusual enrichments in Fe provide evidence for expanded anoxia in the oxygen-
146 minimum zones of Proterozoic oceans, while the enhancement of siderite instead of pyrite
147 deposition at about 800 Ma points to a decline in the extent of euxinic conditions significantly
148 before the deep ocean became oxygenated (Canfield et al. 2008; Lyons et al. 2009; Johnston et
149 al., 2010).

150 Partin et al. (2010) document both U concentration and Th/U ratios in black shales over 3.5
151 billion years of Earth history. They describe a significant increase in U content in carbonaceous
152 shales (possibly as nano-precipitates of uraninite and U^{4+} -silicates) shortly after the rise of
153 atmospheric oxygen at ca. 2.32 Ga (Bekker et al. 2004). This change was associated with the

154 mobilization of U^{6+} , which is easily transported in oxidized aqueous complexes, as opposed to
155 Th, which occurs only in the insoluble 4+ valence state. Another study, using Mo content in
156 organic-rich sulfidic shales as a proxy for ocean redox state (Scott et al. 2008), found that Mo
157 content in shales increased at ca. 2.15 Ga, and again, more strongly during the Ediacaran Period
158 (ca. 580 Ma).

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

164

165 **Mineral Diversity**

166 Studies of Earth's increasing mineral diversity through time point to the occurrence of new
167 paragenetic modes, including those related to new tectonic and biological mechanisms. Grew and
168 Hazen (2009, 2010a, 2010b) and Grew et al. (2011) reviewed the distribution through time of the
169 minerals of beryllium and boron (Figure 3), two quintessential lithophile elements with average
170 crustal abundances of 2.1 and 17 ppm, respectively (Rudnick and Gao 2004). The 108 approved
171 mineral species containing essential beryllium include 66 silicates, 28 phosphates and arsenates,
172 9 oxides and hydroxides, 4 borates, and one carbonate. Beryllium minerals are found most
173 abundantly and in greatest diversity in granitic pegmatites, alkaline and peralkaline pegmatites,
174 hydrothermal deposits associated with volcanic and shallow-level plutonic rocks, and skarns,
175 whereas non-metasomatic metamorphic occurrences are minor and sedimentary occurrences
176 unknown except for placers. Beryllium is a trace element, and therefore minerals containing

177 essential Be appear only after extensive differentiation, which explains the relatively late first
178 appearance of Be minerals in the geologic record. Based on reported finds, the oldest Be
179 minerals are Mesoarchean, when two species formed at the Gravelotte emerald deposit in $2969 \pm$
180 17 Ma granitic pegmatites associated with a greenstone belt in South Africa (Poujol 2001). Ten
181 more species are found in later Meso- and Neoproterozoic (2860 to 2550 Ma) granitic pegmatites
182 and granulite-facies rocks of the Pilbara and Yilgarn cratons, Australia, and the Bird River
183 Province, Canada. Two species in peralkaline rocks and a metamorphic occurrence on the
184 Yilgarn craton bring the total of Archean Be minerals to 15. Anatectic pegmatites in the
185 ultrahigh-temperature Napier complex, Antarctica, introduce three more species in the earliest
186 Paleoproterozoic, the last to appear before a burst of 28 new species towards the close of the
187 Paleoproterozoic (~1850-1715 Ma) in both pegmatites (e.g., Norrö, Sweden; Tysfjord, Norway;
188 Tiptop, South Dakota; Red Ace, Wisconsin) and complex skarn deposits of the Långban type in
189 Sweden. From about 1700 Ma to <1 Ma, the number of new Be minerals increased relatively
190 steadily, with a pulse of 14 new species at 1160 Ma (Ilímaussaq peralkaline complex,
191 Greenland). All of the “principal” episodes of Be mineralization cited by Barton and Young
192 (2002) occurred after 1600 Ma. Barton and Young (2002) cautioned that most Be deposits are
193 concentrated at shallow levels in the Earth’s crust, and thus older occurrences could have been
194 lost to erosion. Conversely, there are some minerals that formed only once or a few times in the
195 course of Earth’s history and have not been reported from other areas, e.g., joesmithite and
196 harstigitite from the Långban-type deposits in Sweden.

197 The 241 valid and 22 prospective mineral species containing essential boron include one
198 nitride, four fluorides, and 258 oxygen compounds (borates) of which 129 contain only $B\Phi_3$
199 triangles and/or $B\Phi_4$ tetrahedra, where $\Phi = O, OH$, and 129 contain additional oxyanionic

200 complexes of Be, C, Si, P, S, or As. Volcanic and sedimentary processes, together with regional
201 metamorphism and overall greater crustal abundance, concentrated boron sufficiently for B
202 minerals to appear earlier in the geologic record than beryllium minerals. The tourmaline species
203 dravite and schorl from the Isua greenstone belt, Greenland (3800 Ma) are the oldest B minerals
204 reported, but earlier formation of B minerals, including evaporitic phases, cannot be excluded, an
205 issue having implications for stabilization of prebiotic organic compounds (Grew et al. 2011).
206 The next oldest minerals to be reported are bonaccordite and two more tourmalines (foitite and
207 magnesio-foitite) in the Barberton greenstone belt, South Africa (3230 Ma) and a Cr-tourmaline
208 in the Singhbhum craton, India (3100 Ma). Highly differentiated 2520-2670 Ma granitic
209 pegmatites and their exocontacts, 2680-2700 Ma hydrothermal activity associated with gold
210 deposits, and ca. 2800 Ma metamorphic rocks of Fiskensæset, Greenland brought the total to 20
211 species in the Archean. The borate deposits in Liaoning and Jilin provinces, China with ca. 2050
212 Ma metamorphism; Mn skarns in the ca. 1825 Ma Långban-type deposits, Sweden; ca. 1950 Ma
213 skarns in the Tayozhnoye deposit, Russia; and ca. 2000 Ma granitic pegmatites and granulite-
214 facies metamorphic rocks of the Magondi belt, Zimbabwe contributed 32 new species in the late
215 Paleoproterozoic, whereas Mn deposits and Mg skarns were largest contributors to 36 more
216 species in the remainder of the Proterozoic. However, the most species, 175, are reported to first
217 appear in the Phanerozoic, including 37 species in Mg skarns and 20 in alkaline rocks.
218 Evaporites, fumaroles, and secondary minerals in extreme desert environments contributed
219 another 82 species. However, these ephemeral B minerals could have also formed much earlier
220 and, with rare exception, failed to survive later geologic events (Grew et al. 2011). The only
221 borate reported from a Precambrian evaporite is chambersite ($Mn_3B_7O_{13}Cl$) associated with algal
222 dolostone in the 1500 Ma Gaoyuzhuang Formation, China (Fan et al. 1999; Shi et al. 2008).

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

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

239

240 **Relative Abundances of Minerals**

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

246 Special attention has also been focused on changes in clay mineralogy, both in absolute and
247 relative terms (Kennedy et al. 2006; Elmore 2009; Tosca et al. 2010). Of note is the massive
248 compilation of Ronov and colleagues (1990), who documented relative clay mineral abundances
249 from approximately 10,000 dated shale samples collected across the Russian Platform – a
250 remarkably large, yet potentially idiosyncratic data set representing the past 1.3 billion years.
251 Sverjensky et al. (2010) demonstrate that these data, which reveal dramatic fluctuations in the
252 relative proportions of kaolinite, chlorite, montmorillonite, and illite, correlate with variations in
253 atmospheric O₂ and CO₂, as well as with the rise of deep-rooted vascular plants after 400 Ma and
254 the appearance of associated ectomycorrhizal fungi (symbiotic root-associated fungi with hyphae
255 that penetrate the soil) at ~200 Ma (Taylor et al. 2009; see Figure 4).

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

261

262

A MINERAL EVOLUTION DATABASE

263 Mineral evolution studies involve correlating mineralogical variables with time and evolving
264 geologic setting. Extensive tabulations of mineral species and localities (notably
265 <http://mindat.org>) have proven critical in this effort. However, the principal impediment to
266 advancing studies of mineral evolution is the lack of a comprehensive database that links such
267 mineral species and locality information with ages and geologic context. Much of the necessary
268 geochronological data exist in the literature, but in widely scattered primary sources.

269 Consequently, documenting the age distribution of a single mineral species may require locating
270 ages of several thousand localities in dozens of countries.

271

272 **Database Development**

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

280 This large-scale effort finds an illustrative analog in the Paleobiology Database
281 (<http://paleodb.org/cgi-bin/bridge.pl>), an international, community-based project to make fossil
282 occurrence data available to all paleontologists. To date, data have been entered for more than
283 170,000 taxa and nearly 100,000 collections. As discussed below, this large and growing
284 database not only enables paleontologists to track taxa and assemblages through time (and across
285 environments), but also to normalize sampling in ways that reduce the distorting effects of
286 collection bias (e.g., Alroy et al., 2008; Kiessling et al., 2010; Peters and Heim 2010; Alroy
287 2010).

288 Mindat.org has been running online since October 2000 and is now the largest online database
289 of mineralogical information. The core purpose of mindat.org is to record information about
290 mineral localities worldwide, to list the reported and verified mineral species at these localities,
291 and, where possible, to provide photographs of these localities and their mineral specimens.
292 There are currently over 20,000 registered users on mindat.org, of whom several hundred active

293 contributors submit data and photographs for the project. A management team of approximately
294 25 members helps to verify new submissions, and a discussion forum allows the wider
295 community to question and validate new postings.

296 The mindat.org website is based on the open source PHP and MySQL systems, using custom
297 software developed primarily by Jolyon Ralph. This software will be updated to allow age
298 information to be entered for use in this mineral evolution project. An advantage of employing
299 the Mindat platform is that data can be exported easily to and from other mineral databases, such
300 as GEOROC (<http://georoc.mpch-mainz.gwdg.de/georoc>) and PetDB (<http://www.petdb.org>).

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

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

315

316 **Data Mining Software Development**

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

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

329

330

UNANSWERED QUESTIONS IN MINERAL EVOLUTION RESEARCH

331
332
333 Mineral evolution represents an alternative way to frame mineralogy – an approach that
334 complements more traditional presentations of the subject based on solid-state chemistry and
335 physics. Certainly there is considerable pedagogical power in presenting mineralogy in the
336 context of the narrative sweep of Earth history, including nebular evolution, planetary accretion
337 and differentiation, initiation of plate tectonics and continent formation, the evolving
338 composition of the atmosphere, the origins of life, and the evolution of varied biochemical
339 pathways and ecological niches. But does mineral evolution offer anything new as a predictive
340 methodology? Is there anything that might guide mineralogical research in new directions?

341 The key to development of a long-range mineral evolution program is to examine previously
342 unrecognized temporal trends in mineral properties and distributions by adding the time
343 dimension to mineralogical studies. Here we explore several promising unanswered questions,
344 each of which presents avenues for research that would be facilitated by the proposed mineral
345 evolution database.

346
347 *1. Are there temporal trends in the first appearances and cumulative numbers of mineral*
348 *species?* A database with all localities and their ages for the >4500 known mineral species will
349 enable analysis of the diversification of Earth's near-surface mineralogy through time. Studies on
350 the first appearances of minerals of Be and B (Grew and Hazen 2009, 2010a, 2010b) and work in
351 progress on the minerals of Hg, Mo, W, Cu, I, and Br point to possible pulses in their origins.
352 However, a comprehensive database of all mineral locality ages is required to distinguish
353 statistically significant increases in the numbers of mineral species from non-uniform temporal
354 distributions of known mineral localities.

355 One important opportunity is to identify mineral species that are highly sensitive to
356 environmental conditions and, consequently, that reflect aspects of Earth's geochemical,
357 tectonic, and biological evolution. For example, spodumene ($\text{LiAlSi}_2\text{O}_6$) occurs in the 3040 Ma
358 New Consort pegmatites in the Barberton greenstone belt, South Africa (Harris and Robb 1995);
359 these are the oldest known differentiated pegmatites and thus point to early stages of element
360 concentration through partial melting, crystallization, and fluid-rock interactions. Other species
361 such as cassiterite (SnO_2), pollucite [$(\text{Cs},\text{Na})_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot(\text{H}_2\text{O})$], and a number of minerals found
362 in massive sulfide deposits (including rare sulfides and sulfosalts) may also serve as indicators of
363 highly differentiated magmatic and hydrothermal systems, or of multiple recycling of evolved
364 continental crust. High-pressure minerals such as coesite and magnesiodumortierite are largely
365 restricted to crustal rocks subjected to ultrahigh-pressure metamorphism during subduction.
366 Mineral data could thus possibly provide significant constraints on early history of fluid-rock
367 interactions, crustal and mantle dynamics, and the establishment of plate tectonics.

368 Another potentially revealing research topic is to track detrital minerals and the minerals
369 included in them through time. A wealth of relatively low-grade sedimentary rocks, some as old
370 as 3800 Ma, preserve detrital mineral suites that provide forensic data on surface lithologies
371 subjected to erosion. In what may be seen as a precursor study, Taylor and McLennan (1985)
372 used the elemental composition of Archean and Proterozoic shales to infer crustal history. Most
373 previous mineralogical efforts have focused on zircon, but research could be expanded to the
374 whole suite of detrital minerals. For example, Meng (1988) and Meng and Dymek (1987)
375 reported that some metamorphic tourmalines in the 3800 Ma Isua greenstone belt, Greenland
376 have cores inferred to be of detrital origin with compositions plotting in the fields of both
377 metasedimentary and igneous tourmaline (Henry and Guidotti 1985), suggesting the intriguing

378 possibility of tourmaline-bearing continental crust older than the Isua belt. Detrital almandine
379 garnet and kyanite may also reflect Al-rich lithologies indicative of crustal reworking. Muscovite
380 inclusions in Hadean zircon from Jack Hills, Western Australia are interpreted to suggest that
381 magmas hosting the zircon were derived dominantly from anatexis of metasedimentary rocks,
382 i.e., rocks with precursors deposited in a Hadean ocean (Harrison 2009). The preservation of
383 unaltered detrital pyrite, siderite, and uraninite in Mesoarchean fluvial conglomerates has been
384 cited as evidence for an anoxic surface environment in the Archean (Grandstaff 1980;
385 Rasmussen and Buick 1999; Frimmel 2005; Sverjensky and Lee 2010). Studies that compare the
386 first appearance of mineral phases on different cratons represent yet another opportunity to
387 understand Earth's dynamic history.

388 Systematic surveys of the cumulative numbers of mineral species can reveal if there were
389 pulses of mineral formation, waxing and waning of mineral-forming processes, or even episodes
390 of "mineral extinction." As noted above, paleontological surveys of the number and distribution
391 of fossil species, properly corrected for the areal distributions and ages of fossiliferous
392 formations, have revealed dramatic pulses of biodiversification as well as mass extinctions
393 (Sepkoski 1997; Bambach et al. 2004; Alroy et al. 2008; Alroy 2010). Similar statistical
394 treatments of mineral diversity through time hold the promise of revealing analogous patterns in
395 Earth's mineral evolution. Note, however, that unlike the irreversible extinction of biological
396 species, mineral species that disappear from the rock record in one formation commonly
397 reappear elsewhere as old paragenetic conditions are repeated or new paragenetic modes come
398 into play.

399 An important task in this regard is to conduct a survey of the number and areal extent of
400 mineral localities through time in order to document the absolute number or percentage of

401 localities versus time. Any claims of mineral diversification or extinction events must be scaled
402 to such locality/age statistics, as raw occurrence values will reflect, at least in part, the mapped
403 availability of rocks of differing age and geologic setting. For example, geochronologic studies
404 of zircon reveal a general lack of ages between 2.45 and 2.22 Ga, bracketing the time of three
405 major Paleoproterozoic glacial events (Bekker et al. 2005; Condie and Aster 2009). Such gaps in
406 the rock record must be factored into any analysis of mineral diversity through time.

407
408 *2. What do changing mineral assemblages through time reveal about changes in near-surface*
409 *environments?* Mineral occurrences through time may provide sensitive indicators of near-
410 surface geochemical environments, including atmospheric and oceanic chemistry, and could thus
411 serve as monitors of pO_2 and pCO_2 through Earth history. For example, banded iron formations
412 (BIFs) have been cited as especially sensitive indicators of Precambrian geochemistry. Their
413 mineralogy, including relative proportions of magnetite, hematite, iron carbonates, and other
414 phases, as well as their volumetric extents through time, show clear temporal trends that may
415 partly reflect oxygenation of the oceans (Klein 2005; Bekker et al. 2010).

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

421 Evaporite minerals reveal details of terrestrial environments as well as the composition of the
422 stranded water bodies from which they precipitated. For example, jarosite
423 $[(K,Na,H_3O,X^{+1})Fe^{3+}_3(OH)_6(SO_4)_2]$, a family of hydrous iron sulfate minerals, indicates acidity at
424 the time of its formation. Therefore, the discovery of jarosite in >3 Ga sedimentary rocks on

425 Mars may help to illuminate the surface history of that planet (Squyres et al., 2004). Clay
426 minerals are also important in documenting evolution of Earth's near-surface environments
427 (Tosca et al. 2009; Elmore 2009; Sverjensky et al. 2010), including changes in ocean and
428 atmospheric composition, the geochemistry of near-surface aqueous fluids involved in diagenesis
429 and low-grade metamorphism, and the rise of terrestrial biota.

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

445 Ratios of trace and minor elements and isotopes, especially of redox-sensitive elements,
446 represent an important opportunity for further research. Temporal studies of variations of Th/U
447 in black shales (Partin et al. 2010) and Re/Mo in molybdenite (McMillan et al. 2010) over 3

448 billion years of Earth history demonstrate that elemental ratios can prove to be sensitive
449 indicators of changes in Earth's near-surface environment related to geochemical and
450 biochemical evolution. The isotopic compositions of Fe and Mo in sedimentary rocks also
451 provide tools for reconstructing the redox history of seawater (e.g., Rouxel et al. 2005; Anbar
452 and Rouxel 2007; Dahl et al. 2010). Several common minerals and mineral groups, including
453 biopyriboles (i.e., amphiboles, pyroxenes, and micas), garnet, spinel, chlorite, and tourmaline,
454 possess crystal structures that can accommodate dozens of different chemical elements.
455 Systematic investigation of minor and trace elements in these minerals through time could reveal
456 trends that reflect the emergence of new modes of fluid-rock interaction, changes in ocean and
457 atmospheric chemistry, and the influences of living systems.

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

462
463 *3. What are the complete lists of minerals from given periods of Earth history and do those*
464 *lists reveal distinctive environmental characteristics of those periods?* As we obtain age
465 information for a significant fraction of all known mineral localities, it would be instructive to
466 compare the mineral diversity through the different eras of Earth history. For example, what are
467 implications of the dozen or so known Hadean mineral species preserved as inclusions in ancient
468 zircons, and do those minerals possess distinctive chemical or isotopic characteristics? Do
469 minerals reflect the biological innovations of the Archean Eon's four Eras (Eoarchean, 3.85-3.6
470 Ga; Paleoarchean, 3.6-3.2 Ga; Mesoarchean, 3.2-2.8 Ga; and Neoproterozoic, 2.8-2.5 Ga) – a time
471 when life arose and metabolic processes such as nitrogen fixation and photosynthesis evolved?

472 Similarly, how is the rise of atmospheric oxygen in the Paleoproterozoic Era (2.5-1.6 Ga)
473 reflected in Earth's near-surface mineral diversity? More recently, is the rise of land plants or the
474 late Mesozoic expansion of flowering plants reflected in changing mineralogy?

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

483 Clay minerals present a particularly intriguing and challenging case of mineral survivability.
484 Reports of clay minerals are sparse for rocks older than the Late Archean (e.g., Tosca et al.
485 2010). Does the paucity of older clay minerals primarily reflect their lack of durability (i.e., an
486 inherently short mineralogical half-life) or rather was there also a significantly reduced clay
487 mineral production prior to 2.5 Ga? Are clay minerals in older rocks original, or were they
488 formed more recently by alteration? Why are ancient clay minerals apparently preserved so well
489 on Mars (Ehlmann et al. 2008), at least compared with the terrestrial environment? In the
490 absence of plate tectonic activity, can clay minerals survive for eons in near-surface
491 environments?

492 In considering the complete inventory of minerals from a given geologic age, it is also
493 intriguing to consider the distribution of trace and minor elements. Prior to the first minerals of
494 Be and B, where did these elements reside? Were they present as dispersed trace elements in

495 other phases, either in solid solution or in defects? Did they concentrate along grain boundaries,
496 and if so in what form? Are there as yet unrecognized nano-phases? These questions, which
497 could be pursued for example through the nanoscale study of chondrites, are tied closely to
498 traditional concerns of crystal chemistry and the first appearances of varied cation polyhedral
499 and other structural motifs of the mineral kingdom.

500
501 *4. For a given mineral species, what is the age distribution of all known samples; were there*
502 *periods of increased or reduced rates of mineral formation?* It is possible that geochemical,
503 tectonic, or biological events may be manifested in the increased production or suppression of
504 certain key mineral species. A comprehensive survey of all known occurrences of a species
505 through time might thus reveal pulses or gaps. For example, a plot of the approximately 4000
506 known localities of molybdenite versus time, especially if coupled with trace and minor element
507 data and correlated with paragenetic mode, might reveal details of near-surface oxygenation,
508 bioavailability of Mo, the initiation of nitrogen fixation by the Mo-bearing nitrogenase enzyme,
509 and other key events. Furthermore, regional variations in these data might reveal otherwise
510 hidden aspects of paleogeography and tectonic history.

511
512 *5. What can we learn from changes in crystal morphology through time?* The crystal habits of
513 minerals can be strongly influenced by environmental factors, including temperature, pressure,
514 composition of aqueous solutions, and biological activities (Babel 1990; Cody and Cody 1991;
515 Orme et al. 2001; Pope et al. 2000). Calcite (CaCO_3), for example, is known to occur in dozens
516 of distinct crystal forms – variations that may reveal much about environmental conditions (Teng
517 and Dove 1997; Teng et al. 1998, 2000). Many different organisms precipitate calcite or
518 aragonite in tests and shells (e.g., Stanley and Hardie 1998; Knoll 2003), and still others facilitate

519 or inhibit CaCO_3 nucleation and growth due to the chemical properties of their metabolic
520 products or the physicochemical properties of organic exudates (Pentacost 2005). Systematic
521 surveys of calcite crystal morphology, therefore, might reveal previously unrecognized trends in
522 environmental conditions, including ocean chemistry, hydrothermal systems, and biological
523 innovations.

524
525 *6. Can minerals provide unambiguous biosignatures (or “abiosignatures”) in our search for*
526 *life on other worlds?* Hazen et al. (2008) concluded that approximately two-thirds of known
527 mineral species on Earth are the indirect consequence of biology, mostly as a consequence of the
528 GOE. If so, then many mineral species may provide an unambiguous signature of a living world.
529 Minerals from the oldest rocks may help to constrain which minerals were involved in the origin
530 of life (Papineau 2010) and prove to be robust and easily detected in the search for
531 extraterrestrial life. That said, we must be cautious, as the expanded repertoire of minerals
532 actually reflects the availability of oxygen, not minerals synthesized solely or even principally by
533 organisms. On Mars the presence of oxides and sulfides reflects redox conditions at and near the
534 planetary surface, whether or not biology influenced those conditions.

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

540

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

CONCLUSIONS

543
544
545 What does mineral evolution have to offer that is new? Plots of the diversity of mineral
546 species through time have proven to be an important first step, as they appear to reveal pulses of
547 mineral formation (and possible “extinction”) that point to important changes in Earth’s near-
548 surface environment. However, a comprehensive data base that records ages and geologic setting
549 for all known mineral localities will allow much more varied and subtle questions to be
550 addressed. For example, the significance of mass-independent S isotope effects was only realized
551 after several dozens of S isotope analyses were plotted versus time (Farquhar et al. 2000),
552 whereas the observation of subtleties in the zircon $\delta^{18}\text{O}$ record required more than 1000 data
553 points (Valley et al. 2005). With access to a comprehensive Mineral Evolution Database and
554 flexible data mining procedures, numerous other questions of this kind could be posed. Thus, the
555 Mineral Evolution Database could lead to original research studies that are difficult to undertake
556 in any other way.

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

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ACKNOWLEDGMENTS

569 We are grateful to Russell Hemley and the Carnegie Institution for Science for a generous
570 grant to support initial development of the Mineral Evolution Database. We thank Claude
571 Herzberg and an anonymous reviewer for constructive comments. This work was supported in
572 part by the NASA Astrobiology Institute. Additional support for D.A. Sverjensky and R.M.
573 Hazen was provided by a NSF-NASA Collaborative Research Grant to the Johns Hopkins
574 University and the Carnegie Institution for Science. D.A. Sverjensky also acknowledges support
575 from DOE Grant DE-FG02-96ER-14616.

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FIGURES AND CAPTIONS

882
883 Figure 1. Plot of $\Delta^{33}\text{S}$ values versus age for sulfide and sulfate minerals. Inset shows $\Delta^{33}\text{S}$ values
884 versus sample age for evaporite minerals and carbonate-associated sulfate. The disappearance of
885 significant mass independent sulfur isotope fractionation in the past 2.4 billion years has been
886 linked to the rise of a UV-shielding ozone layer during the Great Oxidation Event, and the
887 variation in the $\Delta^{33}\text{S}$ of oceanic sulfate (inset) is interpreted to reflect changes in the microbial
888 ecology of the oceanic sulfur cycle (data sources include Farquhar et al. 2000, 2002, 2007; Hu et
889 al. 2003; Ono et al. 2006, 2009; Mojzsis et al. 2003; Bekker et al. 2004, 2009; Johnston et al.
890 2005, 2006, 2008; Whitehouse et al. 2005; Ohmoto et al. 2006; Papineau and Mojzsis 2006;
891 Cates and Mojzsis 2006; Papineau et al. 2005, 2007; Bao et al. 2007; Philippot et al. 2007;
892 Kaufman et al. 2007; Kamber and Whitehouse 2007; Ueno et al. 2008; Partridge et al. 2008).
893 (Courtesy of James Farquhar)

894
895 Figure 2. $\delta^{18}\text{O}$ values of zircon grains from 1,200 rocks spanning more than 96% of Earth history
896 (Valley et al. 2005) reveal variations in $\delta^{18}\text{O}$ values that point to the evolution of both crustal
897 recycling and crust-mantle interactions through time. (Courtesy of John Valley.)

898
899 Figure 3. Plot of the reported oldest occurrences of 107 Be minerals of 108 total (the age for
900 jeffreyite could not be established from the available data) and 263 B minerals based on
901 literature search (Grew and Hazen unpublished data). The plot is cumulative because each
902 reported new appearance is added to the number of minerals having been reported prior to the
903 age of the appearance. The plot is not meant to indicate the totality of minerals forming in the

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

906

907 Figure 4. Ronov et al. (1990) documented relative clay mineral abundances from approximately
908 10,000 shale samples collected across the Russian Platform, representing the past 1.3 billion
909 years. Sverjensky et al. (2010) noted that fluctuations in relative clay abundances over the past
910 600 million years correlate with variations in atmospheric O₂ and CO₂. For example, the relative
911 abundance of chlorite in shales tracks values of the level of atmospheric O₂ inferred from the
912 GEOCARBSULF model. (Red labels represent abbreviations for geological time intervals.) The
913 deviations from this correlation in the past 200 million years might reflect the rise of mycorrhizal
914 fungi. (Courtesy of Dimitri Sverjensky)

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