1   **Revision 2**

2   **Mineralogy, materials science, energy, and environment – A 2015 perspective**

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8   **Abstract**

9   Mineralogy is both a basic and applied discipline, basic in understanding, on the atomic

10   scale, the structure, properties, and reactivity of minerals and applied in its relevance to geology,

11   planetary processes, environmental issues, and materials in the broader sense. This article is a

12   2015 snapshot of the interrelations and opportunities linking mineralogy and such other fields.

13   The emphasis is on showing how relevant, indeed essential, mineralogy is to the stewardship of

14   our planet in the broadest sense.

15   **Introduction**

16   Mineralogy has always been inspired by the beauty of minerals and their structures and

17   the wonder of the natural world. At the same time it has been nourished by practical applications

18   - all inorganic materials we use in technology, from Stone Age spear points to silicon age

19   semiconductors, come from minerals. Think of it, the guts of your cell phone started as sand,

20   with dabs of iron ore, rare earth minerals, and lots of organic compounds derived from

21   petroleum. If we run out of these ingredients, or if we soil our surroundings with their production

22   and disposal, we are in trouble. Thus knowledge of mineralogy forms the underpinning, not just

23   for technological advancement and big bucks, but also for stewardship of our planet. Realizing

24   our responsibility as scientist citizens as well as researchers, I write this review to point out the

25   symbiotic relationships among mineralogy, technology, and environmental issues and to

26   highlight opportunities for the future of our field. Though public policy and politics are

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27   inexorably linked to science and technology, they are not a major focus of this paper. Because

28   this article is short, the references cited are not extensive and have been chosen, when possible,

29   to themselves be of a review or overview nature.

30   Clearly there are many other points of intersection between mineralogy and materials

31   science. Both fields are blurring the distinction between organic and inorganic, with hybrid

32   materials, biomineralization, microbial synthesis of technological materials, and the use of

33   functionalized nanoparticles in medicine being some areas of active interest. Both fields utilize

34   magnetic properties for functionality and indication of sample processing or geologic history.

35   Both are increasingly cognizant of environmental impacts and the role solids (industrial

36   pollutants and natural minerals) play in catalyzing and directing chemical reactions in both

37   aqueous and atmospheric environments. The present paper presents only a few examples of such

38   commonality.

39   **The Porous Interface between Mineralogy and Materials Science**

40   Both mineralogy and materials science study solid inorganic compounds - oxides,

41   silicates, chalcogenides, carbonates, carbon polymorphs, sulfates, halides and others. Both fields

42   determine structure, physical properties, and stability of the materials. The main goal of

43   mineralogy as part of earth science is to use such fundamental knowledge to better understand

44   the conditions of formation of the minerals through space and time, with pressure as well as

45   temperature being major variables. Mineralogists consider slow processes occurring on a

46   geologic time scale as well as processes occurring in the laboratory. The goal of materials

47   science, broadly speaking, is to use basic knowledge of solid state compounds and their

48   properties to design and tailor materials with technologically useful functionality. Minerals are

49   often complex solid solutions containing many elements at major, minor, and trace

50   concentrations. Materials are synthesized at controlled and usually simple compositions, with

51   impurities (dopants) intentionally introduced to fine-tune properties such as electrical

52   conductivity. Despite these differences in emphasis, the two fields share many commonalities.

53   Both often study similar families of materials, e.g. perovskites, spinels, garnets, zeolites, iron and

54   manganese oxides. Both fields require fundamental understanding of structure, bonding, and

55   thermodynamic properties. Both make use of modern experimental and computational

56   methodologies. With these commonalities in mind, this review points out areas of overlap,

57   synergy, and complementarity and opportunities for future interactions.

58

59   **Concepts, Techniques, Centers**

60   A simplistic picture of the relation between mineralogy and materials science is that the

61   mineralogist sits at the feet of the solid state physicist to learn fundamental concepts and to take

62   advantage of modern instrumentation. The reality has always been much more of a two way

63   street, with mineralogy (or mineral physics) leading the way in a number of areas. Historically,

64   the needs of the lunar science program accelerated the development of the electron microprobe

65   and other instrumentation. Mineralogists have been at the forefront of electron microscopy since

66   the 1970s. The most obvious direction in which mineralogy leads is in the application of pressure

67   as a variable, absolutely necessary to understand planetary interiors. Diamond anvil cell (DAC),

68   methodology has grown to span conditions from shallow hydrothermal systems to the center of

69   the Earth (Bassett 2009). At the same time the development of multianvil press technology, first

70   in Japan and now worldwide, has led to tremendous advances in synthesis and property

71   measurements of phases under mantle conditions (Liebermann 2011). Hand in hand with high

72   pressure development has been the invention of diagnostics suitable to very small sample

73   volumes - especially diffraction and spectroscopy utilizing synchrotron radiation (Liebermann

74   2011). Thus the mineralogy community has led the development and operation of synchrotron

75   beam lines for high pressure research. This mineralogical emphasis on high pressure led to the

76   NSF funded Science and Technology Center in High Pressure Research (CHiPR) which

77   functioned for eleven years (1991-2002) and to its successor, COMPRES (Consortium for

78   Materials Properties Research in the Earth Sciences), currently providing support for

79   mineralogical synchrotron research and related projects.

80   Several DOE (Department of Energy) Energy Frontier Research Centers (EFRC), led by

81   mineralogists or geochemists were funded in 2009-14 and recently renewed for the next four

82   years. The EFRCs (46 centers in 2009-14 and 32 in 2014-18) emphasize fundamental

83   multidisciplinary collaborative research with eventual energy applications. The strong

84   participation of the mineralogy/mineral physics community in these highly competitive centers is

85   testimony to the high quality of our research and offers unique educational opportunities for

86   students, postdocs and faculty.

87   Shock wave research (Jeanloz et al. 2007; Ahrens et al. 2009) probes an even wider set of

88   planetary conditions and also forms a bridge between planetary science, national defense

89   interests, materials science, and cosmology. It is part of a broader field known collectively as

90   high energy density science (HEDS) which is being propelled forward by technological advances

91   such as the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (Moses

92   et al. 2009) and new free electron laser facilities worldwide. HEDS spans a pressure regime from

93   planetary interiors to stars to nuclear explosions and brings together mineral physicists, planetary

94   scientists, material scientists, cosmologists, and nuclear physicists.

95   Mineralogists continue to take advantage of developments in crystallography,

96   revolutionized by ever-increasing computer power. The ability to perform single crystal

97   refinements on ever smaller crystals, the combination of synchrotron and neutron experiments

98   (and in some cases simultaneous fitting of data), the emphasis on whole powder pattern fitting

99   including diffraction intensity between Bragg peaks, which gives information on disordered

100   solids – all these enable efficient solution of previously intractable problems (Ehm et al. 2007;

101   Parise 2006; Skinner et al. 2013;). Electron microscopy continues to prosper, with high

102   resolution compositional analysis an exciting development (Botton 2007; Kotula et al. 2014;

103   Sanchez et al. 2010; Walther et al. 2014). X-ray spectroscopies probing local and short range

104   order continue to develop (Beyer et al. 2014; Chapman and Chupas 2013). Yet describing

105   structure and partial order on the 1-100 nm scale still remains challenging. Neutron scattering

106   and diffraction techniques have improved greatly, requiring much less sample and providing

107   crystallographic, magnetic and vibrational data (Loong 2006; McMahon 2012; Redfern 2002;

108   Ross and Hoffmann 2006). The sensitivity of neutrons to light elements, including hydrogen,

109   makes them complementary to X-rays. In situ studies at high temperature and/or high pressure

110   are an emerging frontier for both mineralogical and materials studies.

111   Another area of mineralogical leadership is in structural, kinetic, and thermodynamic

112   characterization of reactions at the solid - aqueous interface. Earth scientists have pioneered

113   neutron and synchrotron-based spectroscopic and diffraction techniques to study such reactions

114   and have closely coupled experiment and computation (see, for example Fenter et al. 2007;

115   Kumar et al. 2009; Spencer et al. 2009; Strongin et al. 2010; Wang et al. 2014; Zhang et al.

116   2014). Mineral dissolution and precipitation occurs at the mineral-water interface, and the

117   processes controlling both dissolution and precipitation often involve nanoparticles and clusters.

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118 Mineralogists have led the way in realizing that there is a continuum between dissolved aqueous

119 ions, polyoxometallate and carbonate clusters in solution, amorphous and crystalline nanoparticle

120 precipitates, and bulk solid phases (Gebauer and Cöelfen 2011; Nyman and Burns 2012; Ohlin et

121 al. 2010; Radha and Navrotsky 2013; Rustad and Casey 2012).   Such understanding is crucial

122 not just for geochemistry and environmental science but for the many industrial processes which

123 occur in aqueous environments, often at somewhat elevated temperatures. These include

124 materials synthesis (including of zeolites for catalysis in the oil industry), catalysis itself, CO_2

125 sequestration, and the longevity and degradation of devices such as batteries, fuel cells, and

126 sensors.

127   The mineralogical/geochemical community has long used isotopes to date rocks and

128 study their sources. Recent advances which simultaneously enable chemical and isotopic

129 compositions to be determined with high spatial resolution (Ferry et al. 2014, Valley et al. 2014)

130 open new opportunities to follow mineral reactions at the nanoscale, probe equilibrium or lack

131 thereof, and study kinetics. These methods are barely known to the materials community, yet

132 would find many applications there.

133   A wealth of new materials has been created by materials scientists. Using techniques

134 involving low temperature processing, vapor phase deposition, ion exchange, and various

135 precursor routes, metastable materials can be explored and applied. Freed from the "tyranny of

136 equilibrium", one is able to access not just the lowest free energy phase assemblages, but a dense

137 energy landscape of only slightly metastable structures. Such new materials have unique optical,

138 electronic, magnetic, and catalytic properties. Two examples of new classes of materials are

139 superconductors with high critical temperatures (Oesterreicher 2007; Ren and Zhao 2009;

140 Tretyakov et al. 2004), and silica zeolites and mesoporous materials (Asefa and Tao 2012;

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141   Broach 2010; Han and Zhang 2012; Li and Yu 2014). This emphasis on metastable materials

142   puts new focus on seeking and characterizing metastable natural materials, for example the

143   myriad polymorphs of manganese and iron oxides, which in turn may have useful properties.

144   At the same time the focus on other planets both in the solar system and beyond

145   (Buchhave et al. 2014), has freed mineralogists from the "tyranny of Earth's geotherm and

146   composition". Mineralogists are no longer constrained to think only within the pressure –

147   temperature – composition parameter space on Earth, but can contemplate very different

148   planetary conditions and new materials - lakes of hydrocarbons, planets with diamond-rich

149   interiors, high energy density interiors verging on nuclear fusion, interior water-rich oceans

150   below icy surfaces, the harsh conditions for dust grains in space -to name a few. Is this a

151   renaissance for petrology?

152   New materials and minerals require new data, including thermodynamic properties.

153   Commercial thermal analysis equipment has expanded to fill a wider temperature range and

154   many instruments combine measurements to include not just mass and heat as a function of

155   temperature (classical TGA-DSC) but also evolved gas analysis (EGA) by mass spectrometry or

156   infrared spectroscopy, structural measurements by X-ray diffraction, and other tandem

157   techniques (Gabbott 2008; Mojumdar et al. 2009). Low temperature heat capacity measurements,

158   needed to obtain standard entropies of phases have been made much more accessible, both in

159   terms of smaller sample size and more rapid measurement, through the Quantum Design PPMS

160   system, with specific techniques developed to handle small amounts of powdered mineral

161   samples (Dachs and Benisek 2011; Shi et al. 2011). The high temperature Calvet twin

162   microcalorimeter used for heat of formation measurements by oxide melt solution calorimetry,

163   previously only home-built, has been commercialized as the Setaram AlexSYS (Levchenko, et

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164   al. 2009).   Experimental thermodynamics is poised for a renaissance, both to obtain needed data

165   on new materials and to interface with computational studies, including the national Materials

166   Genome Initiative, EarthCube, and other "big data" endeavors.

167   A number of workshops have been held in the materials community, and recently in the

168   geoscience community related to the Materials Genome Initiative. The mineralogical community

169   participates in mineralogical and crystallographic data base projects and is active in the creation

170   of websites and programs for easy retrieval of crystallographic data and depiction of mineral

171   structures for both research and educational purposes. Several thermodynamic databases and

172   associated computational programs for mineralogical systems have been developed and, to some

173   extent, maintained and made more compatible with modern information technology (Asimow

174   and Ghiorso 1998; Boudreau 1999; Gualda et al. 2012). These thermodynamic data bases are

175   different from those used by the materials community (the CALPHAD approach) (Bale et al.

176   2009; Becker et al. 2014; Campbell et al. 2014; Kroupa 2013) especially in terms of how solid

177   solutions and melts are modeled. The materials community has limited capability to include high

178   pressure in their data bases and computations. Each community has developed data bases and

179   computational capability for aqueous solutions; yet linking complex mineral (or ceramic) phase

180   thermodynamics and aqueous activity models, especially at high temperature and pressure,

181   remains challenging. There is a great opportunity for the materials and geoscience communities

182   to work together.

183   An even broader challenge is retrieving (data mining) all the known properties of a given

184   material or mineral or ceramic composite or rock, including original experimental data, both

185   recent or in the older literature. It is technologically possible to give any material a code number

186   which would then be used to link it to all other data (or references) on the same material. Should

187 this be done, how, by whom, paid by whom? These are big data questions for the future in both

188 earth and materials science. They also have major implications and impacts for the evolving field

189 of journal publishing. There is no doubt we are living through the biggest communications

190 revolution since the invention of the printing press.

191   Below I give several examples of research bridging mineralogy (mineral physics) and

192 materials science and some outlooks for the future.

193

194   **Perovskites**

195   The perovskite structure (see Figure 1 and Mitchell 2002 for a comprehensive review) is

196 ubiquitous in both materials and Earth science. Materials scientists are still largely unaware that

197 $MgSiO_3$ perovskite may be the single most abundant mineral in our planet, though largely

198 inaccessible because of its instability at ambient conditions. When I lecture on this topic as part

199 of a materials science seminar, it is often a "whole new world" to the materials community and

200 one can hear a pin drop in the lecture hall. Nor are they aware of the detailed high pressure

201 studies of equations of state and phase transitions that the mineral physics community has

202 developed and how these are useful in understanding chemical bonding and benchmarking

203 theoretical calculations. On the other hand, mineralogists still tend to use the term "defect"

204 qualitatively and ignore the rigorous treatment of defect equilibria developed over many years by

205 the materials community. Tailoring the defect chemistry of perovskites by ionic substitution

206 (doping) and control of oxidation state is leading to new perovskite based materials for

207 applications as diverse as solid oxide fuel cells (Cook and Sammells 1991; Jiang and Li 2009),

208 water splitting and other catalytic reactions (Cava 2000; Ghinga et al. 2011), separation

209 membranes (Fontaine et al. 2008), and high temperature superconductors (Dow and Harshman

210   2002; Park and Snyder 1995) and piezoelectrics (Reany 2007). Of potential importance to the

211   incorporation of water in the deep earth are studies showing that perovskites with oxygen

212   vacancies which are oxide ion conductors can incorporate H_2O and become proton conductors

213   (Norby 2009; Norby et al. 2004). Such ceramics may provide analogue compounds for

214   geophysical studies.

215   The coupling of trivalent ions (Al substituting for Si) may also strongly affect defect

216   chemistry, vacancy concentrations, and water content in deep Earth materials (Navrotsky 1999;

217   Spektor et al. 2011). The discovery based on both theoretical and experimental evidence, of "past

218   perovskite", namely closely related complex structures related to perovskite having slightly

219   higher density (Hirose et al. 2006; Umemoto and Wentzcovitch 2006; Yamanaka et al. 2012) has

220   disproved the previously common notion that, at high pressure, crystal structures become simpler

221   and more symmetric. The changing spin state of Fe^{2+} at high pressure adds complexity to

222   structure, bonding, and properties at conditions of the lower mantle and core (Badro 2012). Thus

223   high P-T mineralogy (mineral physics) continues to discover new phenomena.

224   In fine grained (nanophase) materials, additional water incorporation and proton

225   conductivity is associated with grain boundaries (Scherrer et al. 2013). Such observations may

226   help define questions for grain boundary structure and water diffusion in mineralogical systems.

227   In materials science detailed studies of grain boundaries, especially in metals, has led to the

228   concept of "complexions" (Cantwell et al. 2014). These are specific grain boundary structures,

229   seldom more than a few nanometers thick, and having compositions and order different from the

230   bulk material. Different complexions may occur at different grain boundaries in the same

231   material, and they may control transport and reactivity. Though not separate phases, complexions

232   are structurally distinct from their matrix. The ability to characterize these structures and their

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233   compositions by modern electron microscopy opens a new field, probably as important to

234   minerals as to ceramics.

235   Current and future new directions in ceramics have been summarized in a recent review

236   article resulting from an NSF workshop (Rohrer et al. 2012). The challenges and opportunities

237   described there are clearly applicable to the study of minerals as well.

238

239   **Nanophase Materials**

240   In the low temperature aqueous environment minerals often precipitate as fine particles

241   (nanophases) and remain fine-grained without coarsening for long periods of time. Similarly, in

242   chemical synthesis on a laboratory or industrial scale, initial nanophase precipitates are

243   amorphous, or poorly crystalline and only gradually transform to coarse grained stable phase

244   assemblages with heating. Nanomaterials of interest to both mineralogy and materials science

245   include aluminum and iron oxides, titania, and silica. Deposition of solids from a dilute gas

246   phase in technological processes such as chemical vapor deposition and precipitation of mineral

247   phases from a dilute gas phase in the early solar system may share common features, particularly

248   the initial formation and persistence of fine grained (nanophase) precipitates different in structure

249   and properties from bulk materials. A recent development is the realization that differences in

250   surface energies between different phases adds a term to the free energy of reaction in the

251   nanoregime large enough to lead to crossovers in polymorph stability and shifts in the P-T

252   locations of both dehydration and redox equilibria when the system is constrained from

253   coarsening (Navrotsky 2011; Navrotsky et al. 2008, 2010). An example for manganese oxides

254   (Birkner and Navrotsky 2012) is given in Figure 2. This interplay of thermodynamics and

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255   kinetics, with thermodynamics playing a larger role than previously thought, has implications for

256   fields ranging from catalysis to soil science.

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258   **Confinement and Host-Guest Interactions**

259   It is becoming increasingly clear that molecules confined near a solid surface interact

260   strongly with it and exhibit different properties from the same molecules in an unconfined state

261   (Gubbins et al. 2011, 2014; Srivastava et al. 2011; Werner et al. 2014). The solid surface may be

262   roughly planar or it may be strongly faceted or curved. Confinement may occur in two

263   dimensions (at a mineral-water interface) or in three (inside a pore). In the latter case one calls

264   the porous material the host and the confined molecules the guest. The pores may be of specific

265   sizes and arranged in a periodic array within a crystalline material (see Figure 3), such as a

266   zeolite, mesoporous material, or metal organic framework (MOF) (Davis 2014; Furukawa et al.

267   2013; Lehman and Larsen 2014; Valtchev and Tosheva 2013). Pores may be separated and

268   relatively inaccessible or bridged by channels with "windows" of a given size connected in one,

269   two, or three dimensions. The pore walls may be amorphous but the channels arranged with

270   uniform spacing, as in mesoporous silicas, or pores may exhibit a narrow range of sizes with

271   random geometric distribution, as in controlled pore glass (CPG).   Finally there may be a wide

272   distribution of pore sizes and geometries, as in real ceramics and rocks. The systems with

273   simpler and better characterized pore distributions are valuable models for the more complex

274   "real world" systems. Over the past decade the materials community has been able to synthesize,

275   characterize, and model many such controlled pore materials and begin to understand, at the

276   molecular level, the dynamics of confinement. These same materials offer opportunities for

277   mineralogists to study confinement phenomena relevant to earth science, including the effect of

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278   temperature and pressure over wider ranges than of usual interest to the materials community

279   (Anovitz et al. 2013; Stack et al. 2014).

280   Though H_2O is the most common guest molecule, others are of importance to both

281   mineralogy and materials science. Chief among these are CO_2 in the context of carbon dioxide

282   capture and sequestration and CH_4 in the context of natural gas (de Paolo et al. 2013; Guyot et al.

283   2011). In the suite of DOE EFRCs funded from 2009 to 2014, two concerned CO_2 sequestration

284   and one CO_2 capture by MOFs have been renewed and one more added for the next four years.

285   Collaboration between mineralogy, materials science, and petroleum engineering is needed to

286   understand and improve enhanced oil recovery, hydraulic fracturing ("fracking") and long term

287   CO_2 sequestration.

288   Both CO_2 and CH_4 figure prominently in the global carbon cycle in the earth's interior

289   and a large international project, the Deep Carbon Observatory (DCO) funded by the Sloan

290   Foundation brings together research in this field. The scope is broad and includes mineralogy,

291   petrology, and mineral physics. A focus is how carbon is incorporated in the mantle and core,

292   with many unanswered questions as to both the amounts of carbon in these reservoirs and its

293   mineralogical form. Nanodiamonds and other carbon allotropes (Gogotsi and Presser 2014), the

294   incorporation of carbon into solid and molten silicate phases, possibly as C substituting for O

295   rather than Si (Sen et al. 2013), represent additional interfaces between mineralogists and

296   materials science researchers.

297   **Strategic and Critical Materials**

298   There is growing concern at many levels of government that our technology is vulnerable

299   both to real scarcity and to geopolitical constraints in the availability of so-called critical

300   elements (Normile 2010). These include the rare earths, lithium, tellurium, and others. From the

301   point of view of mineralogy, important rare earth minerals, or phases into which rare earths

302   substitute, include bastnäsite, monazite, pyrochlore, and apatite. Lithium comes largely from

303   pegmatite minerals. The demand for rare earths in electronics, cell phones, lighting (LEDs),

304   magnets, and other applications is increasing rapidly, while the growth of the lithium ion battery

305   threatens to outstrip supply, especially if such batteries become commonplace in automobiles.

306   Our vulnerability can be minimized at many different levels: more efficient and environmentally

307   friendly mining and ore processing; finding substitutes or using less of a critical material for a

308   given device; recycling. The National Science Foundation has identified Sustainable Chemistry

309   (SUSchem) as an internal initiative and the Department of Energy has established a "Hub", the

310   Critical Materials Institute, a large program spanning from basic science to industrial

311   intervention and involving national lab, academic, and industrial partners. Because all critical

312   materials come from the Earth and are eventually returned to it as waste, it is clear that

313   mineralogists, materials science researchers, and industry must work together to achieve goals of

314   sustainability in critical materials. Though the details will evolve, these issues will be with us for

315   the foreseeable future.

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317

318   **The Nuclear Fuel Cycle**

319   Whatever the long term future of nuclear energy, electricity-producing reactors will be

320   active in many countries for many years to come, and the safe disposal and stewardship of

321   nuclear waste remains a major issue. (Weber et al. 2009). Natural uranium minerals (uraninite

322   and various complex U^{6+} uranyl pahses) are mined and processed into nuclear fuel, usually UO_2.

323   After use in a reactor, the fuel rods ("spent fuel") are either reprocessed or stored. Safe storage,

324   whether on the surface or in an underground repository, requires the minimization of corrosion

325   and dissolution of UO_2. Earth scientists, materials scientists, and nuclear engineers must work

326   together, and all must work within the geopolitical and policy context to make progress possible.

327   The expertise of mineralogists in solving complex crystal structures has expedited the

328   characterization of the structures of the myriad of uranyl minerals and recently discovered

329   uranium peroxide cluster compounds (Burns 2010; Nyman and Burns 2012). Their reactivity in

330   the environment is critical to understanding uranium transport, including after a reactor accident

331   (Burns et al. 2012). As one considers repositories other than Yucca Mountain for nuclear waste,

332   there is need for much additional work. The recent incident at WIPP, the Waste Isolation Pilot

333   Project in salt formations in New Mexico, highlights the need for additional careful research of

334   waste behavior in different geologic environments. New reactor designs (e.g. small modular

335   accident resistant reactors) and different fuel cycles (e.g. the thorium-based cycle) all require

336   new interdisciplinary collaborations.

337

338   **Outlook**

339   The study of earth materials is evolving to include a much broader spectrum of societally

340   relevant problems and to utilize a more diverse palette of experimental and computational

341   approaches. Our stewardship of a sustainable planet requires deep understanding of geochemical

342   cycles both in the critical zone and in the whole planet. Technology relies on minerals as sources

343   of common, rare, and critical elements and eventually returns these elements to the environment.

344   The richness of mineralogy in extraterrestrial environments is just beginning to be appreciated.

345   Life depends on minerals and influences their formation and transformation. Indeed minerals

346   change through geologic history, and mineral evolution and the emergence of life may be closely

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347 connected (Hazen and Papineau 2012). As mineralogists in the 21st century, we have the good

348 fortune of working in a broad field of both marvelous intellectual challenge and critical societal

349 importance. Our challenge is to choose the most important problems, work with our colleagues

350 in a variety of disciplines to solve them, and to educate the public at all levels as to why

351 understanding materials in the Earth is critical to sustaining both our standard of living and the

352 planet as a whole.

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616 **Figure Caption**

617 Figure 1 The perovskite structure, stoichiometry ABO_3, consists of a linkage of BO_6

618 octahedra sharing corners. The volume defined by the interstices formed by this linkage contains

619 a large B cation, depicted here as the Earth to show the importance of this structure for mineral

620 physics and geophysics. For smaller A cations, the octahedra can tilt, as shown, lowering the

621 symmetry from cubic to tetragonal, orthorhombic or monoclinic.

622 Figure 2 "Phase equilibra in the Mn-O system for (left) bulk materials and (right) 10 nm

623 hydrous nanoparticles. Note expansion of stability field of the spinel, Mn_3O_4 (hausmannite) at

624 the nanoscale. These shifts in phase boundaries reflect the influence of surface energy for high

625 surface area materials. The surface energy of Mn_3O_4 (the spinel hausmannite) is lower than those

626 of Mn_2O_3 (bixbyite) and MnO_2 (pyrolusite). Thus the spinel (with both Mn^{2+} and Mn^{3+}) is

627 thermodynamically stable to higher oxygen fugacity at a given temperature for small particles.

628 (Birkner and Navrotsky 2012). The uncertainties in calculated pressures at a given temperature

629 are on the order of 0.1 log unit, so the shifts for nanoparticles are far beyond experimental

630 uncertainty."

631 Figure 3 Energetics of zeolites, mesoporous silicas and metal organic frameworks (MOF)

632 relative to dense phase assemblages as a function of molar volume. It is striking that a large

633 increase in volume (over a factor of two) caused by the formation of open channels and cages,

634 has a relatively small energy penalty (<30 kJ/mole). This energetic accessibility accounts for the

635 large number of possible structures, described as a "dense energy landscape" (Hughes et al.

636 2013).

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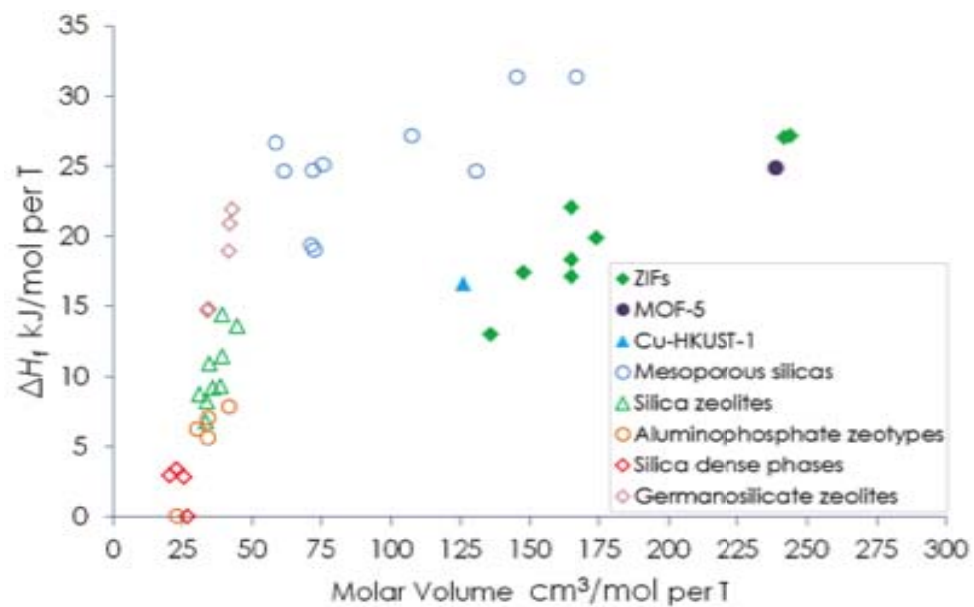639   **Figure 1**
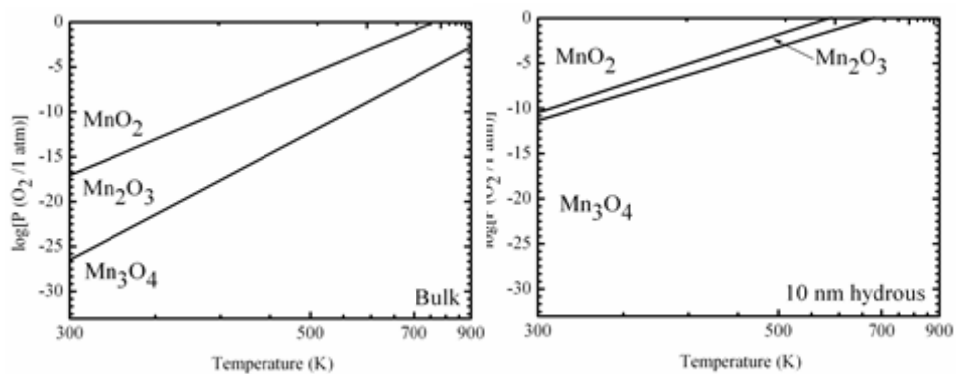
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641   **Figure 2**

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654 **Figure 3**