26 November 2017—Submitted to *American Mineralogist*

HIGHLIGHTS AND BREAKTHROUGHS

Titan mineralogy: A window on organic mineral evolution

Robert M. Hazen[1,*]

[1]Geophysical Laboratory, Carnegie Institution for Science,

5251 Broad Branch Road NW, Washington, DC 20015, USA.

Every planet and moon experiences mineral evolution—a change in the diversity and distribution of minerals through billions of years of physical, chemical, and (in the case of Earth) biological processes (Zhabin, 1981; Hazen et al., 2008; Hazen and Ferry, 2010). A question often pondered in this context asks if minerals exist somewhere in the cosmos that are not found on Earth. As Maynard-Casely et al. (2017) have elegantly shown, one needs look no farther than Saturn's moon Titan for the answer—a resounding "Yes!" They paint a vivid picture of a frozen world perpetually at 92 K, where hydrocarbon rains splash on a landscape of organic-rich rocks containing a rich taxonomy of molecular crystals—ices of water and ammonia, cage-like clathrates hosting small guest molecules, varied organic hydrates, and novel "co-crystals" that incorporate two or more molecular species in stoichiometric ratios.

Multiple paragenetic processes likely enrich Titan's postulated mineralogy. Changes of state from the orange organic-rich atmosphere to liquid and solid phases are important drivers of near-surface distillation and diversification. For example, condensation of tholins, complex molecules

---

***E-mail:** rhazen@ciw.edu

Keywords: mineral evolution; Titan; organic minerals; Hadean mineralogy; origin of life

rich in C, N, and H produced by photochemistry in Titan's atmosphere, are likely to result in a range of colorful crystals (Cable et al., 2011). Hydration reactions may be common, as water molecules from aqueous "cryo-volcanoes" react with organic species. Phase transitions featuring molecular orientational order-disorder reactions could lead to dramatic changes in density and hardness, as well as in electrical and elastic properties. Some organic molecular species would dissolve in Titan's hydrocarbon seas, only to subsequently form exotic evaporite deposits (imagine fields of shiny faceted acetylene crystals sprouting along the margins of hydrocarbon lakes during a Titan "dry spell").

Yet, in spite of the exotic carbon-rich chemistry and alien environmental conditions, Titan has revealed familiar geological features not unlike those of Earth: rivers and lakes, dunes and deltas, mountains and valleys, and those curious cryovolcanoes that erupt aqueous "magmas." Maynard-Casely *et al.*'s contribution emphasizes the diverse physical and chemical properties of purported Titan minerals—their hardnesses, which may contribute to resistant landforms; their melting points, which result in varied fluid-rock interactions, both on the surface and in the warmer Titan interior; and their relative densities and elastic properties that play essential roles in creating and evolving Titan's intriguing topography.

As Maynard-Casely *et al.* emphasize, the study of organic crystal chemistry and phase equilbria at modest pressures and cryogenic conditions—the experimental petrology of Titan—is in its infancy. Consequently, we can anticipate the discovery of many new plausible Titan minerals—as yet unknown carbon-bearing crystalline phases that must surely occur on countless cold, carbon-rich worlds throughout the cosmos.

Earth's organic mineralogy in space and time

Does Titan's intriguing organic mineralogy hold lessons for the story of Earth? At first blush the two worlds have little in common. Not only is Earth warmer and wetter, but the bulk compositions are strikingly different, as well. The crustal mineralogy of our planetary home is dominated by eight elements—oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium comprise 98 percent of the mass? Carbon, by contrast, is a minor constituent, accounting for less than 0.1 weight percent of Earth's crust, and almost all of that carbon is locked into vast precipitated platforms of carbonate minerals (Reeder, 1983; Hazen et al., 2013a). Nevertheless, Maynard-Casely *et al*.'s study inspires a closer look at Earth's organic mineral evolution.

More than 50 "organic minerals" have been identified on Earth (Perry et al., 2007; Downs, 2016; Hazen et al., 2013a), all of which are indirectly derived from biology, including crystals formed by the subaerial alteration of excrement (especially in cave guano deposits), from decaying vegetation and animal matter, or derived from coal and oil shale (e.g., Nasdala and Pekov, 1993; Perry et al. 2007; Hummer et al., 2017), most notably as crystals that condense from a hot vapor phase near burning coal mines (Oftedal, 1922; Rost, 1942; Belakovskiy, 1998; Chesnokov et al., 2008; Witzke et al., 2015; Pekov et al., 2016). Occurrences of these few dozen organic minerals are rare and localized; in several cases species are known from just a few microscopic crystals (mindat.org). Benner et al. (2010; personal communications), furthermore, emphasize that the most common of these compounds are highly oxidized oxalates and carboxylates—phases that consequently possess meager nutritional value on our oxygen-saturated world. Most crystals of more reduced organic species represent food and are thus likely to be consumed almost as soon as they form. The few notable edible exceptions, such as the aluminum benzenehexacarboxylate mineral, mellite, may owe their survival to their low solubilities.

However, early in Earth's history at a time when carbonaceous chondrites and icy comets laced with organics rained with regularity onto the sterile surface, in the prebiotic age before the opportunistic predation of any stray food-like molecule by cellular life, there may have existed a profusion of now extinct organic mineral species (Benner et al., 2010). An inventory of such primordial organic minerals—phases overlooked in prior surveys of carbon mineral evolution (Hazen et al., 2013b) and a preliminary list of potential Hadean mineral species (Hazen, 2013)—is fertile ground for speculation.

Several intriguing crystalline organic compounds not found on Earth today have been invoked in origins-of-life scenarios, both on Earth (Benner et al., 2010) and early Mars (Benner et al., 2000). Prior to the origins of life, these bio-building blocks may have accumulated in concentrated crystalline form until they reached useful amounts. Benner et al. (2010) focus on reactive carbohydrates and related nitrogen-bearing compounds, while Ritson and Sutherland (2013) point to the possible role of crystalline ferrocyanide in the assembly of RNA. The Sutherland group has also studied the facile crystallization of 2-aminooxazole, a plausible prebiotic mineral that could have been an intermediate compound on the pathway to RNA synthesis (Powner et al., 2009; Szostak, 2017).

In addition, early Earth may have boasted a rich variety of crystalline or otherwise self-organized forms of lipids, aromatic compounds, and amino acids, some of which may have precipitated as chirally pure "left-" and "right-handed" crystalline forms (Springsteen and Joyce, 2004; Hein et al., 2011)—a key and as yet poorly understood step from geochemistry to biochemistry (Lahav, 1999; Hazen, 2005). Organic minerals may have abounded in zones where crystals grew from evaporating organic-rich fluids or condensed from a hot gas phase. This geological selection and concentration of life's essential ingredients through crystallization of early Earth's diverse organic milieu is a problem ripe for continued discovery.

Organic mineralogy of the Anthropocene Epoch

Earth's organic mineral evolution is far from being over. The modern age of human exploitation of carbon-rich coal, oil, tar sands, and other hydrocarbon-rich "fossil" fuels—a time dubbed by some advocates the "Anthropocene Epoch"—has seen an explosion in the diversity and distribution of both inorganic and organic solids at or near Earth's increasingly engineered surface (Zalasiewicz et al., 2013; Hazen et al., 2017). Our geological era is marked by the synthesis of millions of diverse organic compounds, some of which will persist in crystalline or polymeric forms for eons. However we choose to characterize those diverse products of human ingenuity—minerals or mineraloids or "mineral-like" phases—solid organic compounds have once again, and for the first time since the prebiotic Hadean Eon, risen to a place of prominence in the chemistry of Earth's near-surface environment.

ACKNOWLEDGEMENTS

I am grateful to Steven Benner, Jack Szostak, and Craig Schiffries for valuable comments and discussions. This publication is a contribution to the Deep Carbon Observatory. Studies of mineral evolution and mineral ecology are supported by the Deep Carbon Observatory, the Alfred P. Sloan Foundation, the W.M.Keck Foundation, the John Templeton Foundation, NASA, a private foundation, and the Carnegie Institution for Science.

REFERENCES CITED

Belakovskiy, D.I. (1998) A natural mineralization process resulting from in situ self-ignition and burning of coal. Abstracts for the Plenary Lectures, Symposia, and Special Sessions of the 17th General Meeting of the International Mineralogical Association, August, 9-14, 1998, Toronto, Canada.

Benner, S. A., Devine, K. G., Matveeva, L. N., and Powell, D. H. (2000) The missing organic molecules on Mars. Proceedings of the National Academy of Sciences, 97, 2425-2430.

Benner, S. A., Kim, H.-J., Kim, M.-J., and Ricardo, A. (2010) Planetary organic chemistry and the origins of biomolecules. In: The Origin of Life, 4th Edition. Deamer, D., Szostak, J. W. Cold Spring Harbor Press. pp. 67-87.

Cable, M.L., Hörst, S.M., Hodyss, R., Beauchamp, P.M., Smith, M.A., and Willis, P.A. (2011) Titan tholins: Simulating Titan organic chemistry in the Cassini-Huygens era. Chemical Reviews, 112, 1882-1909.

Chesnokov, B.V., Shcherbakova, Y.P., and Nishanbayev, T.P. (2008) Minerals of the burned dumps of the Chelyabinsk coal basin. Russian Academy of Sciences, Urals Division Institute of Mineralogy, Miass, Russia. 139 pages (in Russian).

Downs, R.T. (2006) The RRUFF project: An integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan, O03-13.

Hazen, R.M. (2005) Genesis: The Scientific Quest for Life's Origins. Joseph Henry Press: Washington, DC.

Hazen, R.M. (2013) Paleomineralogy of the Hadean Eon: A preliminary list. *American Journal of Science*, **313**, 807-843.

Hazen, R.M and Ferry, J.M. (2010) Mineral evolution: Mineralogy in the fourth dimension. Elements, 6, 9-12.

Hazen, R.M., Papineau, D., Bleeker, W., Downs, R.T., Ferry, J., McCoy, T., Sverjensky, D.A., and Yang, H. (2008) Mineral evolution. American Mineralogist, 93, 1693-1720.

Hazen, R.M., Downs, R.T., Jones, A.P., and Kah, L. (2013) The mineralogy and crystal chemistry of carbon. In R.M. Hazen, A. Jones, and J. Baross [Editors]. *Carbon in Earth.* Washington, DC: Mineralogical Society of America, pp.7-46.

Hazen, R.M., Jones, A.P., Kah, L., and Sverjensky, D.A. (2013b) Carbon mineral evolution. In R.M. Hazen, A.P. Jones, and J. Baross [Editors]. *Carbon in Earth.* Washington, DC: Mineralogical Society of America, pp.79-107.Hazen, R.M. (2016) Carbon mineral ecology.

Hazen, R.M., Grew, E.S., Origlieri, M, and Downs, R.T. (2017) On the mineralogy of the "Anthropocene Epoch." American Mineralogist, 102, 595-611.

Hummer, D.R., Noll, B.C., Hazen, R.M., and Downs, R.T. (2017) Crystal chemistry of abelsonite, the only known crystalline geoporphyrin. American Mineralogist, 102, 1129-1132.

Hein, J.E., Tse, E., and Blackmond, D.G. (2011) A route to enantiopure RNA precursors from nearly racemic starting materials. Nature Chemistry, 3(9), 704–706.

Maynard-Casely, H.E., Cable, M.L., Malaska, M.J., Vu, T.H., Choukroun, M., and Hodyss, R. (2018) Prospects for mineralogy on Titan. American Mineralogist, 103, in press.

Lahav, N. (1999) Biogenesis. Oxford University Press: Oxford, UK.

Nasdala, L. and Pekov, I.V. (1993) Ravatite, $C_{14}H_{10}$, a new organic mineral species from Ravat, Tadzhikistan. European Journal of Mineralogy, 5, 699-705.

Oftedal, I.W. (1922) Minerals from the burning coal seam at Mt. Pyramide, Spitsbergen. Resultater av de Norske Statsunderstottede Spitsbergenekspeditioner, 1, 9-14.

Pekov, I.V., Chukanov, N.V., Belakovskiy, D.I., Lykova, I.S., Yapaskurt, V.O., Zubkova, N.V., Shcherbakova, E.P., and Britvin, S.N. (2016) Tinnunculite, IMA 2015-021a. CNMNC Newsletter No. 29, February 2016, page 202; Mineralogical Magazine, 80, 199-205.

Perry, R.S., Mcloughlin, N., Lynne, B.Y., Sephton, M.A., Oliver, J.D., Perry, C.C., Campbell, K., Engel, M.H., Farmer, J.D., Brasier, M.D., and Staley, J.T. (2007) Defining biominerals and organominerals: Direct and indirect indicators of life. Sedimentary Geology, 201, 157-179.

Powner, M.W., Gerland, B., and Sutherland, J.D. (2009) Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. Nature, 459, 239-242.

Reeder, R.J. (ed) (1983) Carbonates: Mineralogy and Chemistry. Reviews in Mineralogy, 11. Mineralogical Society of America: Washington, DC.

Ritson, D.J. and Sutherland, J.D. (2013) Synthesis of aldehydic ribonucleotide and amino acid precursors by photoredox chemistry. Angewandte Chemie International Edition, 52(22), 5845–5847.

Rost, R. (1942) Supplements to the mineralogy of the burning (coal) heaps in the region of Kladno. Rozpravy II. Trídy Ceské Akademie, 52, 1-4 (in Czech).

Springsteen, G. and Joyce, G.F. (2004) Selective derivatization and sequestration of ribose from a prebiotic mix. Journal of the American Chemical Society, 126(31), 9578–9583.

Szostak, J.W. (2017) The origin of life on Earth and the design of alternative life forms. Molecular Frontiers Journal, 1(2), 1-11.

Witzke, T., de Wit, F., Kolitsch, U., and Blaß, G. (2015) Mineralogy of the burning Anna 1 coal mine dump, Alsdorf, Germany, p. 203-240. In Stracher, G.B., Prakash, A., and Sokol, E.V.

(eds.) Coal and Peat Fires: A Global Perspective. Volume 3: Case Studies – Coal Fires. Elsevier: Amsterdam, 786 pp.

Zalasiewicz, J., Kryza, R., and Williams, M. (2013) The mineral signature of the Anthropocene in its deep-time context. In Waters, C.N., Zalasiewicz, J.A., Williams, M., Ellis, M.A., and Snelling, A.M. [Editors], A Stratigraphical Basis for the Anthropocene. The Geological Society Special Publications, 395, 109-117.

Zhabin, A.G. (1981) Is there evolution of mineral speciation on Earth? Doklady Earth Science Sections, 247, 142-144.