

Genesis: Rocks, Minerals, and the Geochemical Origin of Life

Robert M. Hazen, Guest Editor¹



Calcite crystal surfaces may have adsorbed and organized molecules essential to the origin of life.

Life arose on the young Earth as a natural chemical process. More than half a century of experimental research has underscored the dynamic interactions of atmosphere, oceans, and rocks that fostered this ancient transition from geochemistry to biochemistry. Researchers on the origin of life now conclude that rocks and minerals must have played key roles in virtually every phase of life's emergence—they catalyzed the synthesis of key biomolecules; they selected, protected, and concentrated those molecules; they jump-started metabolism; and they may even have acted as life's first genetic system.

KEYWORDS: origin of life, biogenesis, metabolism, genetics, adsorption

INTRODUCTION

Few scientific questions so capture the public imagination, or provoke such lively debate, as how life on Earth emerged. In this issue of *Elements*, four of the most creative minds in origins research present their original insights on the geochemical origins of life. Each author has studied the field in depth, and each has come to an inescapable conclusion: rocks and minerals must have played a pivotal role in the transition from the blasted, prebiotic Earth to the living world we now inhabit.

The contributions of rocks and minerals to life's geochemical origins were not always so well appreciated. The pioneering experiments of University of Chicago graduate student Stanley Miller and his mentor, Harold Urey, revealed that organic molecules essential to biology form abundantly when a simple mixture of reduced gases is subjected to electrical sparks (Miller 1953; Miller and Urey 1959). Within a decade, a growing army of origins chemists followed their lead to synthesize most of life's essential molecules— amino acids, lipids, sugars, and more (Wills and Bada 2000). Their conclusion: the primordial soup was pregnant with life's building blocks (Chyba and Sagan 1992).

MOLECULAR SELECTION

Deep mysteries remained. The vast volume of Earth's early oceans would have hopelessly diluted the concentration of synthetic organic molecules, no matter how abundantly they were produced. How could such dispersed molecules ever combine into self-replicating entities? Any viable origins scenario thus requires a means to select and concentrate just the right molecules from that watery prebiotic broth. Energetic interfaces, such as a primitive oil slick or an evaporating tidal pool (Lasaga et al. 1971; Lahav et al.

1978), provide plausible solutions. But when it comes to energetic organizing surfaces, nothing beats minerals.

The ability of crystalline surfaces to select and organize molecules is beautifully illustrated in the work of Stephen Sowerby and colleagues, who exposed ideally flat cleavage faces of graphite (C) and molybdenite (MoS_2) to solutions of adenine, guanine, and other biologically interesting organic species (Sowerby et al. 1998). Not only are these cyclic molecules

strongly adsorbed to the mineral surfaces, but they also adopt elegant two-dimensional structures (FIG. 1). Such an organized molecular assembly might represent an early step in the emergence of life.

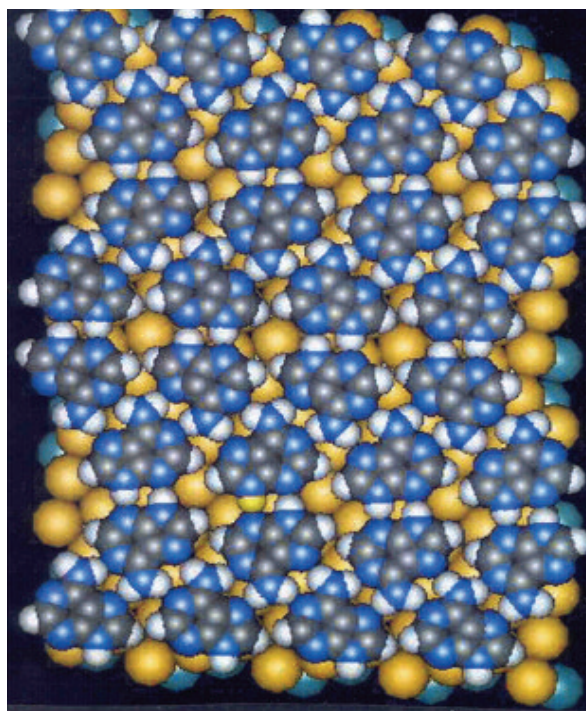


FIGURE 1 Adenine, a biomolecule that contributes to both metabolic and genetic processes ($\text{C}_5\text{H}_5\text{N}_5$; illustrated as clusters of 15 smaller white, silver and blue spheres, which represent hydrogen, carbon and nitrogen atoms, respectively), forms a periodic two-dimensional structure on molybdenite (MoS_2 ; illustrated as larger yellow and blue spheres, which represent sulfur and molybdenum atoms, respectively). Similar molecular adsorption and organization on mineral surfaces may have played a central role in life's origin (after Sowerby et al. 1996).

¹ Geophysical Laboratory, Carnegie Institution and NASA Astrobiology Institute, 5251 Broad Branch Road NW, Washington, DC 20015, USA E-mail: r.hazen@gl.ciw.edu

My own work focuses on the ability of minerals to adsorb interesting biomolecules selectively. One of life's most puzzling biochemical quirks is its high degree of molecular selectivity. Consider amino acids, the building blocks of proteins, as an example. Nature boasts dozens upon dozens of different kinds; more than 70 different amino acids have been extracted from the Murchison meteorite alone. What's more, most amino acids come in mirror image left- and right-handed forms, but for some reason life uses only about 20 of these varied species, and it employs the left-handed kinds almost exclusively.

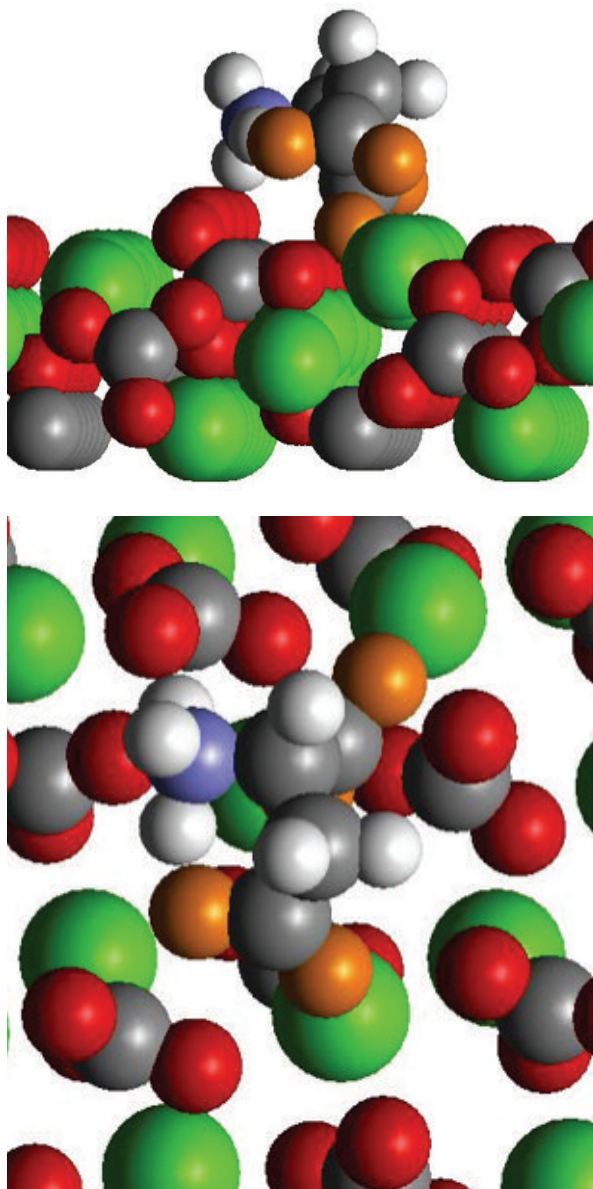


FIGURE 2 A calculated model of aspartic acid adsorption onto the calcite {214} surface reveals three strong interactions: two between Ca in calcite (green spheres) and O in the amino acid (orange spheres), and one between O in the calcite (red spheres) and H in the amino acid (white spheres). Grey and blue spheres represent carbon and nitrogen atoms, respectively. The essential amino acid aspartic acid occurs in both left-handed (L) and right-handed (D) forms, but life uses the L form almost exclusively. Experiments (Hazen et al. 2001) and theoretical calculations (Asthagiri et al. 2004) reveal that the common calcite {214} crystal surface strongly selects for D-aspartic acid, whereas the mirror-image face selects L-aspartic acid.

What process selected this idiosyncratic subset of molecules during the origin of life? A possible answer lies in the behavior of everyday minerals like quartz and calcite, which we find are able to select and concentrate specific biological amino acids from an equimolar mix (Churchill et al. 2004). What's more, certain crystal faces of these and other minerals display an aptitude for adsorbing handed or "chiral" molecules (Hazen et al. 2001; Hazen and Sholl 2003; Hazen 2004, Fig. 2). Perhaps in this way minerals provided the organizing template for life.

METABOLISM AND GENETICS

Among the many lively ongoing debates in origin-of-life research is the conundrum of which came first, metabolism or genetics? Metabolism is the ability to manufacture biomolecules from a source of energy (such as sunlight) and matter scavenged from the surroundings (usually in the form of small molecules). An organism cannot survive and grow without an adequate supply of energy and matter. Genetics, by contrast, is the process by which biological information is transferred from one generation to the next—a blueprint for life via the mechanisms of DNA and RNA. An organism cannot reproduce without a reliable means to pass on this genetic information.

The problem for understanding life's origins is that metabolism and genetics constitute two separate, chemically distinct systems in cells, yet they are inextricably linked in modern life. DNA holds genetic instructions to make hundreds of molecules essential to metabolism, while metabolism provides both the energy and the basic building blocks to make DNA and other genetic materials. Like the dilemma of the chicken and the egg, it is difficult to imagine back to a time when metabolism and genetics were not intertwined. Consequently, origin-of-life researchers engage in an intense, ongoing debate about whether these two aspects of life arose simultaneously or independently and, if the latter, which one came first (Orgel 1986; Morowitz 1992).

Mineralogy offers insights to this debate, for various minerals may have played many different roles in the transition from geochemistry to biochemistry. Modern life, for the most part, provides few clues about this rocky start, but the complex enzymes that promote cellular metabolism may represent a dramatic exception. Biocatalysts in the form of protein enzymes assist metabolic reactions, which build life's essential components from small molecules like H₂O and CO₂. These enzymes commonly incorporate a small cluster of transition metal and sulfur atoms at the so-called "active site," where the critical electron transfer process takes place (Beinert et al. 1997). In many modern enzymes, this metal-sulfur cluster looks just like a tiny bit of sulfide mineral. Building on these observations and a flurry of fascinating theoretical speculations (notably Wächtershäuser 1992), George Cody and coworkers at the Carnegie Institution exploit this intriguing biochemical observation in their studies of sulfide-catalyzed organic reactions at elevated temperatures and pressures—conditions that mimic prebiotic hydrothermal environments. In this issue, Cody explores how such mineral-catalyzed reactions may have jump-started a primitive metabolic cycle. Perhaps the first life-like chemical system was a cycle of metabolic reactions driven by the redox potential of iron and nickel sulfides.

Noted origins expert James Ferris of Rensselaer Polytechnic Institute begins from a different perspective, that of the molecular biologist. Ferris and his colleagues argue that life must have begun with the first self-replicating genetic molecule, such as RNA. His transforming studies of clay-catalyzed formation of RNA polymers have made headlines

and have proven extremely influential in the origins research community. His sweeping review in this issue recounts a quarter-century of progress toward understanding how clay minerals might have adsorbed, selected, organized, and catalyzed the building blocks of life's genetic machinery.

Famed University of Chicago mineralogist Joseph V. Smith, echoing the work of Cody and Ferris, sees minerals as both effective templates for the selection of minerals and likely catalysts for the initiation of biochemical reactions. Smith, however, focuses on zeolites and other mesoporous minerals—materials with molecule-sized pores that are produced abundantly through the action of primordial volcanism.

LIVING CLAYS

And then we come to the extraordinary vision of Glasgow-based Graham Cairns-Smith, who proposes that the emergence of life was not just promoted by a mineral, but that the first lifeform was perhaps a clay mineral itself. Even the most chauvinistic geoscientist might balk at such a claim, but Cairns-Smith's ideas have been taken very seriously by the origin-of-life community, and his almost four decades of provocative publications are among the most widely cited in the field. In elegant and persuasive prose, he suggests that clay minerals carry a kind of genetic information in their complex sequences of point defects, layer orientations, and metal cation substitutions. Clays themselves undergo natural selection and evolution as they dissolve and precipitate, he says. The most "fit" sequences win in this Darwinian struggle for survival. For Cairns-Smith, clay minerals were indeed the first lifeforms on Earth.

In the hands of a lesser scholar, such a proposition might have been rejected out of hand, but Cairns-Smith commands close attention and broad respect. His work is deeply rooted in the philosophy of biology—What is life? he asks, and what characteristics serve to distinguish the living from the dead? All known life today is carbon based, with cellular structures enclosing a DNA-based genetic system, but was that always so, and must it be the same on other worlds? By exploring the life-like properties of hypothetical evolving clays, and by proposing detailed (if as yet technically impossible) experiments, he is squarely in the mainstream of the scientific enterprise.

Scientists are still far from understanding the ancient, intricate processes that led to the origin of life. Fascinating experiments and theories of the sort highlighted in this issue will continue to contribute small pieces to that immensely complex puzzle. As a unified picture of life's origin emerges, the central roles of rocks and minerals are sure to expand and further serve to integrate the seamless web of knowledge that links the physical and biological sciences.

ACKNOWLEDGEMENTS

RMH thanks the four authors for their outstanding efforts in preparing these reviews, and editors Michael Hochella and Pierrette Tremblay of *Elements* for the opportunity to bring this issue together, and for their efficient guidance and support throughout the process. Support for RMH during work on this issue was provided by the NASA Astrobiology Institute and the Carnegie Institution of Washington. ■

REFERENCES

- Asthaigiri, A, Downs RT, Hazen RM (2004) Density functional theory modeling of interactions between amino acids and chiral mineral surfaces. Geological Society of America Abstracts with Programs 36: 153
- Beinert H, Holm RH, Münck E (1997) Iron-sulfur clusters: Nature's modular, multipurpose structures. *Science* 277: 653-659
- Churchill H, Teng H, Hazen RM (2004) Correlation of pH-dependent surface interaction forces to amino acid adsorption: implications for the origin of life. *American Mineralogist* 89: 1048-1055
- Chyba CF, Sagan C (1992) Endogenous production, exogenous delivery, and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* 355: 125-132
- Hazen RM (2004) Chiral crystal faces of common rock-forming minerals. In: Palyi G, Zucchi C, Caglioti L (eds) *Progress in Biological Chirality*, Elsevier, New York, pp 137-151
- Hazen RM, Sholl DS (2003) Chiral selection on inorganic crystalline surfaces. *Nature Materials* 2: 367-374
- Hazen RM, Filley T, Goodfriend GA (2001) Selective adsorption of L- and D-amino acids on calcite: Implications for biochemical homochirality. *Proceedings of the National Academy of Sciences USA* 98: 5487-5490
- Lahav N, White D, Chang S (1978) Peptide formation in the prebiotic era: Thermal condensation of glycine in fluctuating clay environments. *Science* 201: 67-69
- Lasaga AC, Holland HD, Dwyer MJ (1971) Primordial oil slick. *Science* 174: 53-55
- Miller SL (1953) Production of amino acids under possible primitive earth conditions. *Science* 117: 528-529
- Miller SL, Urey HC (1959) Organic compound synthesis on the primitive earth. *Science* 130: 245-251
- Morowitz HJ (1992) *The Beginnings of Cellular Life: Metabolism Recapitulates Biogenesis*. Yale University Press, New Haven, 208 pp
- Orgel LE (1986) RNA catalysis and the origin of life. *Journal of Theoretical Biology* 123: 127-149
- Sowerby SJ, Edelwirth M, Heckl WM (1996) Self-assembly at the prebiotic solid-liquid interface: structure of self-assembled monolayers of adenine and guanine bases formed on inorganic surfaces. *Journal of Physical Chemistry B* 102: 5914-5922
- Wächtershäuser G (1992) Groundworks for an evolutionary biochemistry: the iron-sulfur world. *Progress in Biophysics and Molecular Biology* 58: 85-201
- Wills C, Bada J (2000) *The Spark of Life: Darwin and the Primeval Soup*. Perseus Publishing, Cambridge, Massachusetts, 320 pp ■