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Mineral surfaces and the prebiotic selection and organization of biomolecules

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ABSTRACT

One of the most enigmatic steps in Earth's ancient transition from a lifeless planet to a living world was the process or processes by which prebiotic organic molecules were selected, concentrated, and organized into the essential macromolecules of life. More than a half-century of theory and experiment points to the critical roles of mineral surfaces in the assembly of proteins, lipid bilayers, and genetic polymers. This review considers three aspects of this problem: (1) the self-assembly of lipids, which may be enhanced in the presence of minerals; (2) the role of minerals in polymerization of amino acids and nucleic acids; and (3) the selective adsorption of organic species, including chiral molecules, onto mineral surfaces.

Keywords: Surface studies, calcite, quartz, feldspar, new technique, microarray, origin of life

INTRODUCTION

The origin of life approximately four billion years ago was a geochemical event, dependent on reactions among the Archean oceans, a primitive atmosphere, and rocks and minerals. This hypothesis of "chemical evolution," like any valid scientific model, leads to numerous testable predictions: Life must have emerged as a sequence of chemical steps of increasing complexity, and each of these chemical steps must be subject to confirmation in reproducible laboratory experiments.

This naturalistic view of life's origin, though widely accepted within the scientific community, can evoke as much public controversy as any topic in science. In particular, intelligent design (ID) represents a highly publicized and intensely criticized rival hypothesis to chemical evolution (Scott 2004; Forrest and Gross 2004). According to supporters of the ID model, life is too complex to have arisen by natural chemical processes (Behe 1996; Dembski 1999). Life requires hundreds or thousands of interconnected chemical reactions; consequently, ID supporters find it difficult to imagine a step-wise process from simplicity to complexity. Indeed, according to this view, life is "irreducibly complex." The logical conclusion, according to ID proponents, is that a supernatural designer—either an alien or God—must have engineered life on Earth. In this view, life arose by some combination of natural and supernatural events.

Most philosophers of science argue that intelligent design does not rise to the standards of an acceptable scientific hypothesis, because it relies on supernatural processes to explain the natural world. This dependence on miracles not only invalidates ID as science, but it also represents suspect theology (Miller 1999; Pennock 1999; Fry 2000; Hazen 2005a, 2005b; Bertka 2006). ID relies on the discredited "God in the gaps" argument, by which one resorts to supernatural explanations if a natural phenomenon is seemingly too complex to understand as a lawful process.

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Supporters of ID point to the origin of life as the quintessential example of irreducible complexity. Ultimately, the most powerful response to any God in the gaps argument is to fill in the gaps, in this case by a research program that demonstrates a natural transition from the chemical simplicity of the Hadean Earth to the emergent complexity of the first living cell. If such biological complexity can be shown to arise spontaneously as the result of lawful, natural processes, then the central tenet of ID regarding life's supposed miraculous origin is invalidated.

The objective of this Presidential Address is to outline such a scenario for the origin of life on Earth based on the hypothesis that life's genesis is an example of the more general natural phenomenon of emergent complexity (Holland 1995, 1998; Morowitz 2002; Hazen 2005a). In this summary I place special emphasis on one of the most significant gaps in our present understanding of life's origin—the selection, concentration, and organization of biomolecules into life's essential macromolecules. In particular, I elaborate some of the processes by which mineral surfaces may have facilitated this key emergent step in the ancient transition from geochemistry to biochemistry.

THE EMERGENCE OF LIFE

The origin of life on Earth can be modeled as a sequence of emergent steps, each of which added chemical complexity to the geochemical world (Hazen 2001a, 2005a). Emergent complexity commonly arises in systems of numerous interacting particles, or "agents," as energy flows through the system (Prigogine 1980; Holland 1998; Morowitz 2002). Numerous examples include the shapes of sand dunes and ripples (Bagnold 1941, 1988; Hansen et al. 2001), the formation of galactic spiral structures (Bertin 1980; Carlberg and Freedman 1985), and the behavior of myriad biological systems such as slime mold, ant colonies, and the conscious brain (Solé and Goodwin 2000; Camazine et al. 2001). The emergence of life required at least four such steps: (1) the emergence of biomolecules, (2) the emergence of

macromolecular systems, (3) the emergence of self-replicating cycles of molecules, and (4) the emergence of molecular evolution by natural selection (Hazen 2005a).

The first of these emergent steps, the prebiotic synthesis of biomolecules, is also the best understood. Since the pioneering synthesis studies of Stanley Miller and Harold Urey (Miller 1953, 1955; Miller and Urey 1959; see also Wills and Bada 2000), facile production of organic molecules has been demonstrated for several plausible prebiotic environments (Chyba and Sagan 1992; Lahav 1999; Fry 2000; Hazen 2005a). Amino acids, sugars, lipids, and many other biomolecules have been produced under conditions simulating Earth's Archean atmosphere (Lerman 1994a, 1994b, 1996; Ellison et al. 1999; Dobson et al. 2000; Tuck 2002), mid-ocean hydrothermal systems (Hennet et al. 1992; Marshall 1994; Russell and Hall 1997; Brandes et al. 1998; McCollom and Simoneit 1999; Cody et al. 2000, 2001, 2004), and surface and shallow subsurface environments (Miller and Urey 1959; Oró 1960, 1961; Reid and Orgel 1967; Shapiro 1988, 1995; Wills and Bada 2000), as well as interstellar and nebular environments (Bernstein et al. 1999; Ehrenfreund and Charnley 2000; Dworkin et al. 2001).

More problematic is the second emergent step by which life's idiosyncratic subset of biomolecules was selected and then concentrated from the dilute, diverse suite of prebiotic molecular species that must have accumulated in the primitive oceans. Consider the problem of amino acids. More than 70 different amino acids have been extracted from the carbon-rich Murchison meteorite (Cronin and Chang 1993). This inventory, moreover, contains a mixture of both left- and right-handed amino acids. Life, by contrast, employs only 20 principal amino acids and these molecules occur almost exclusively in their so-called "left-handed" forms. Life's sugars, lipids, and polycyclic molecules exhibit similar molecular selectivity (Nelson and Cox 2004; Hazen 2005a). By what process did this molecular selection and concentration occur?

Mineral surfaces have long been recognized as having the potential to select and organize organic molecules in the path from geochemistry to biochemistry. In 1945 Victor Goldschmidt speculated: "Assemblage on corresponding crystal faces of enantiomorphic pairs of crystals, such as right-hand and left-hand quartz crystals, would provide us with a most simple and direct possibility of localized separate assemblage of right- and left-hand asymmetric molecules" (Goldschmidt 1952, p.101). John Desmond Bernal (1951) expressed similar views in his influential text, *The Physical Basis of Life*, wherein he advocated the special role of clays in life's origins.

In the following sections, I consider three aspects of mineral-mediated molecular selection and organization: (1) the self-assembly of lipids into spherical cell-like structures called vesicles, the formation of which may be enhanced in the presence of minerals; (2) the role of minerals in the polymerization of amino acids and nucleic acids; and (3) the selective adsorption and concentration of organic species, including the challenging problem of chiral molecular selection, onto mineral surfaces.

MOLECULAR SELF-ORGANIZATION

The simplest mode of molecular selection is self-organization, which is a phenomenon displayed most dramatically by

amphiphilic molecules. Amphiphilic molecules possess both hydrophilic and hydrophobic regions—a situation that can lead to spontaneous self-organization in an aqueous environment (Tanford 1978; Deamer and Pashley 1989; Segré et al. 2001; Deamer 2003). The elongated phospholipid molecules that form most cell membranes provide an important example. Each of these molecules has two hydrophobic hydrocarbon chains at one end and a hydrophilic phosphate group at the other. When the concentration of phospholipid molecules in solution achieves a critical minimum value, they then self-organize into vesicles (Fig. 1), which are enclosed bilayer structures with only hydrophilic regions exposed to water (Bangham et al. 1965; Deamer 2003).

Self-organizing lipids have been identified and concentrated from a variety of plausible prebiotic sources of organic molecules (Hazen 2005a). In a landmark study, Deamer and Pashley (1989) extracted a suite of self-organizing amphiphiles from the Murchison carbonaceous chondrite. They concluded: "If amphiphilic substances derived from meteoric infall and chemical evolution were available on the prebiotic earth following condensation of oceans, it follows that surface films would have been present at air-water interfaces. ... This material would thereby be concentrated for self-assembly into boundary structures with barrier properties relevant to function as early membranes" (p. 37). Subsequent synthesis experiments in simulated deep space (Dworkin et al. 2001) and hydrothermal (Hazen 2005a) environments also reveal vesicle-forming fractions.

Similar studies of lipid self-organization by Pier Luigi Luisi and coworkers (Luisi 1989, 2004; Luisi and Varela 1990; Bachmann et al. 1992; Luisi et al. 1994) not only confirm that vesicles form with ease, but also demonstrate that these structures can grow, gradually incorporating new lipid molecules from solution. In some instances, these vesicles have been shown to be autocatalytic—that is, they act as templates that trigger the formation of more vesicles.

These intriguing emergent behaviors have led Luisi to propose the "Lipid World" scenario for life's origin (Luisi and Varela 1990). In this conceptually simple model, prebiotic lipids formed abundantly on Earth and in space. Once in solution, these lipids could have self-organized into cell-like vesicles that captured a primitive genetic molecule—an early, simpler version of DNA or RNA. These experiments are prelude to efforts to make the first synthetic life-form (Bachmann et al. 1992; Szostak et al. 2001).

Lipid self-organization proceeds spontaneously at a critical concentration of amphiphilic molecules, but vesicle formation may be affected dramatically by the presence of minerals. On the one hand, divalent cations (Mg^{2+} and Ca^{2+}) in solution tend to inhibit vesicle formation (Monnard et al. 2002). This finding has led to the extrapolation that life may have had to begin in fresh water, although experiments investigating self-assembly of the full range of plausible prebiotic lipids in salt water have not been explored adequately. On the other hand, Hanczyk et al. (2003) showed that addition of fine-grained clay to a solution with a sub-critical concentration of lipids may trigger the spontaneous formation of vesicles. Subsequent work by Szostak's group (Chen et al. 2004) revealed that a wide variety of powdered minerals promotes similar vesicle formation. Although the mechanisms

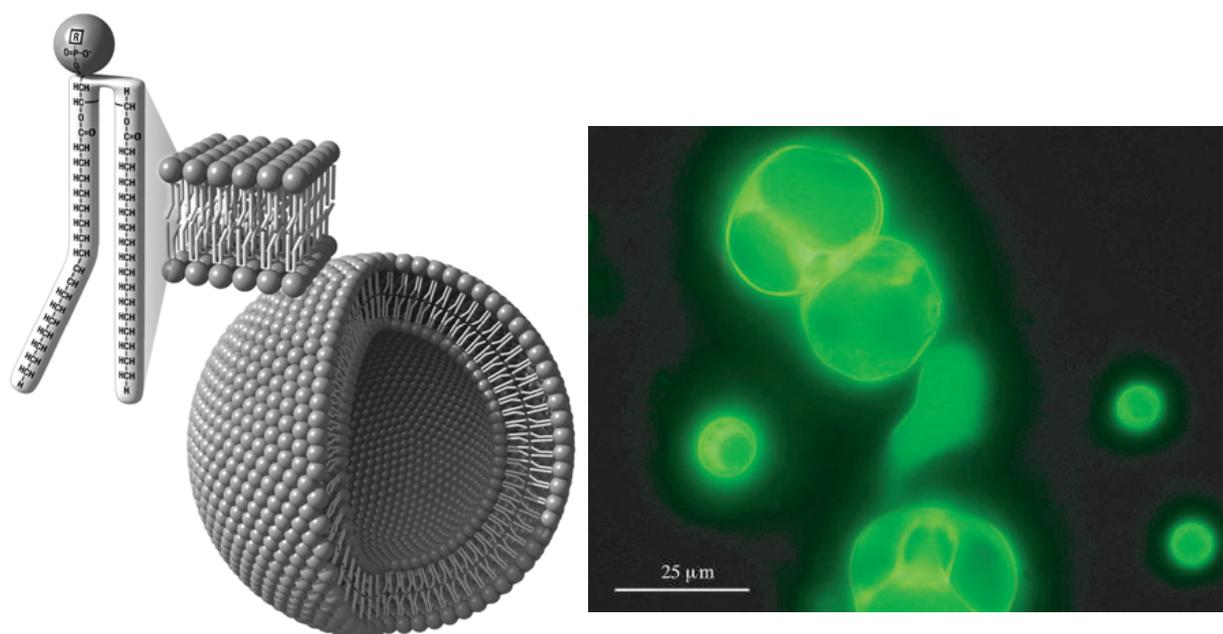


FIGURE 1. The self-assembly of amphiphiles occurs when molecules with both hydrophilic and hydrophobic regions arrange themselves into a minimum energy configuration, such as a spherical phospholipid bilayer vesicle (left-hand drawing from Hazen 2005a, copyright 2005 Wood Ronsaville Harlan, Inc. (used with permission); right-hand image of fluorescent amphiphilic vesicles from Hazen 2005a, courtesy of David Deamer).

of these mineral-molecule interactions are at present unknown, the potential of minerals acting as nucleation sites for molecular organization is well established.

These varied experiments suggest that the self-organization of amphiphilic molecules must have been an important step in the origin of life—a step in which minerals may have played a useful, if not essential, role. However, unlike vesicle-forming lipids, many of the key building blocks of life, including amino acids, sugars, and nucleic acid bases, are highly soluble in water and do not spontaneously self-organize. For these molecules, minerals may have provided a critical template for the formation of biopolymers.

MINERAL-INDUCED POLYMERIZATION

Many of life's essential macromolecules, including proteins and nucleic acids, are chain-like polymers that form from water-soluble monomers. The production of such macromolecules requires two concerted steps: The correct molecules first must be concentrated and then assembled into the desired structure. In the case of the self-organizing lipid membranes reviewed above, these two tasks occur simultaneously and spontaneously; lipids in water separate while they self-organize into a bilayer structure. But other key biological macromolecules, including proteins, carbohydrates, and DNA, form from water-soluble monomeric units—amino acids, sugars, and nucleic acids, respectively. Consequently, these polymers tend to break down, not form, in water.

One promising way to concentrate and assemble organic molecules from a dilute solution is first to concentrate them on a surface. For example, scanning tunneling microscopy reveals that nucleic acid bases, including adenine and guanine, form

ordered two-dimensional structures on ideally flat (001) surfaces of molybdenite (MoS_2) and graphite (Sowerby et al. 1996, 1998a, 1998b, 2002; Uchihashi et al. 1999).

For decades, the prevailing paradigm has been that the molecules of life assembled at or near the ocean-atmosphere interface. The surface of a calm tidal pool, or perhaps a primitive slick of water-insoluble molecules, might have promoted such molecular assembly (Lasaga et al. 1971; Morowitz 1992). However, these surface environments may be exposed to the damaging effects of lightning storms and ultraviolet radiation, which tend to break down biopolymers.

For more than half a century, origin-of-life researchers have recognized that rocks and minerals provide attractive alternative surfaces for molecular concentration and assembly. British biophysicist John Desmond Bernal (1951) advocated the special role of clay minerals. The proclivity of clays to exhibit a surface electrostatic charge enhances their ability to adsorb organic molecules, while their tendency to occur in fine-grained particles provides relatively large reactive surface areas.

Subsequent experiments have supported Bernal's speculations. Lahav et al. (1978) discovered that amino acids concentrate and polymerize on clay minerals to form small, protein-like molecules. Such reactions occur when a solution containing amino acids evaporates in the presence of clays—a situation not unlike the evaporation that might have repeatedly dried up shallow prebiotic ponds or tidal pools.

More recently, James Ferris and colleagues at Rensselaer Polytechnic Institute have induced clays to act as scaffolds in the formation of RNA, the polymer that carries the genetic message enabling protein synthesis (Ferris 1993, 1999, 2005; Holm et al. 1993; Ferris and Ertem 1992, 1993; Ertem and Ferris

1996, 1997). Their studies reveal that activated RNA nucleotides in solution are relatively unreactive until clay minerals are added. Then, in a matter of hours, oligomers 10 nucleotides long assemble, and in two weeks, 50-nucleotide fragments are recovered. The fine-grained clay particles induce polymerization, though the molecular-scale mechanisms of the process are not yet fully understood.

In similar experiments, Salk Institute biologist Leslie Orgel and colleagues have employed both clay minerals and hydroxylapatite to form a variety of protein-like chains of amino acids up to several dozen molecules long (Ferris et al. 1996; Hill et al. 1998; Liu and Orgel 1998). Orgel also developed a theory of “polymerization on the rocks,” in which he pointed out both the promise and problems associated with molecular assembly on mineral surfaces (Orgel 1998; Acevedo and Orgel 1986). Minerals such as clays and hydroxides are able to adsorb relevant biomolecules, including amino acids and nucleotides. Furthermore, once two molecules are adsorbed close to each other, they have a tendency to polymerize. As more molecules are added to a lengthening polymer, however, the strand becomes more tightly bound to the mineral surface. Orgel concluded that such strong adhesion might prove problematic in the production of useful biologically active macromolecules.

Jack Szostak and Harvard University colleagues, who mixed clays, RNA nucleotides, and lipids in a single experiment, revealed one possible solution (Hanczyc et al. 2003). The clays not only adsorb RNA, but they also hasten the formation of lipid vesicles. In the process, RNA-decorated clay particles are incorporated into the vesicles. This spontaneous self-assembly of RNA-containing vesicles represents a plausible pathway to the emergence of a self-replicating cell-like entity.

Joseph V. Smith and coworkers (Smith 1998; Parsons et al. 1998; Smith et al. 1999; Smith 2005) have explored an intriguing mineralogical alternative to adsorption on clays by invoking reactions within the channels of zeolites. The tendency of some hydrocarbon molecules to enter zeolite channels points to the kind of facile molecular selection and organization required for life’s origins. Smith proposed that prebiotic molecules concentrated inside zeolite channels; once packed with a long column of molecules, a zeolite mineral might have promoted additional reactions, including polymerization.

The most elaborate mineral-based origins scenario, initially proposed by A. Graham Cairns-Smith in 1964, posits that self-replicating clay minerals were, themselves, the first living entities. According to this model, aperiodic cation distributions or random layer stacking sequences constitute a kind of genetic information, analogous to the sequence of nucleotides (A, T, G, and C) in DNA. Cairns-Smith speculated that clay minerals “replicate” by cleaving. Furthermore, more favorable (i.e., stable) sequences evolve at the expense of less favorable sequences through the selective processes of growth and dissolution of individual particles. Ultimately, he speculated, organic molecules used clay-life as scaffolding for the evolution of modern biochemistry (Cairns-Smith 1968, 1977, 1982, 1985a, 1985b, 2005; Cairns-Smith and Hartman 1986).

In spite of these varied proposals, all of the aforementioned experimental studies of molecular organization on mineral surfaces employed relatively concentrated solutions of one organic

species. These investigations point to the ability of mineral surfaces to adsorb molecules and promote organic reactions, but they shed little light on the problems of molecular selection and concentration from a dilute prebiotic “soup” of numerous competing organic species. Accordingly, investigation of the selective adsorption and concentration of biomolecules on rock-forming minerals has provided a central theme for much of my recent research into life’s origins.

MOLECULAR SELECTION ON MINERAL SURFACES

Prebiotic synthesis of relevant biomolecules must have been facile, as demonstrated by a half-century of experiments (e.g., Chyba and Sagan 1992; Lahav 1999; Fry 2000; Wills and Bada 2000). Consequently, the prebiotic oceans must have evolved into a dilute solution of thousands of different organic molecular species, most of which played no role whatsoever in life’s origins. A central challenge in origins research, therefore, is elucidation of the next emergent step—efficient mechanisms for selection, concentration, and organization of monomers into life’s macromolecules (Hazen 2001b, 2005a). Accordingly, various common rock-forming minerals have been studied as possible templates for organic adsorption.

Differential molecular adsorption

What factors influence selective molecular adsorption from a complex solution onto a mineral surface? To address this question, Churchill et al. (2004) considered the differential adsorption from amino acid solutions onto various mineral surfaces. Biological amino acids, the building blocks of proteins, feature a central carbon atom linked to one hydrogen atom, one carboxyl group (COOH), one amino group (NH₂), and one of twenty different side groups that confer corresponding differences in physical and chemical properties (e.g., Nelson and Cox 2004).

We find that electrostatic interactions often play a dominant role in interactions between minerals and amino acids. The net charge of each mineral surface is a function of solution pH: The net surface charge of the mineral is zero when the solution pH equals the “point of zero charge,” pH_{pzc} . At $pH_{solution} < pH_{pzc}$, the net surface is positive, whereas at $pH_{solution} > pH_{pzc}$, the net surface charge is negative (Parks 1965, 1984; Davis and Kent 1990; Dzombak and Morel 1990; Eggleston and Jordon 1998). Similarly, amino acids are zwitterions (molecules with both acid and base groups), for which the net molecular charge is also a function of solution pH. The net molecular charge is zero at the “isoelectric point,” pI . At $pH < pI$, the net molecular charge is positive, whereas at $pH > pI$, the net molecular charge is negative.

Churchill et al. (2004) immersed specimens of quartz ($pH_{pzc} = 2.8$), calcite ($pH_{pzc} = 9.5$), and albite ($pH_{pzc} = 2.6$) in equimolar solutions (pH ~ 5, 7, and 9) of six different amino acids, including aspartic acid ($pI = 2.98$), glutamic acid ($pI = 3.08$), glycine ($pI = 6.06$), alanine ($pI = 6.11$), lysine ($pI = 9.74$), and tyrosine ($pI = 5.63$). As expected, maximum adsorption occurred for mineral-molecule pairs with differing pH_{pzc} and pI (Carter 1978; Lowenstam and Weiner 1989; Weiner and Addadi 1997). Thus, of the six amino acids, aspartic acid and glutamic acid adsorb most strongly onto calcite, whereas lysine is the only one of these amino acids that adsorbs significantly onto quartz.

Net electrostatic charge appears to dominate the adsorption behavior in some mineral-molecule systems, such as quartz-amino acids. The highly selective adsorption of lysine onto quartz is significant, for it argues against quartz playing an important role in the prebiotic assembly of functional peptides (which typically require a mix of amino acids). However, electrostatic interactions cannot be the only factor in molecular selection. For example, all six amino acids are adsorbed to a significant degree by calcite, even in the case of lysine, which has an isoelectric point (9.74) similar to calcite's point of zero charge (9.5). Thus, calcite remains a mineral of considerable interest in studies of the prebiotic synthesis of catalytic polymers.

These studies of calcite reveal that factors besides net electrostatic interactions must play a significant role in selective molecular adsorption. Ideally, to elucidate these additional factors, it would be useful to compare pairs of molecules with identical electrostatic properties. Thus, we turn to the enigmatic problem of life's homochirality.

Origins of biochemical homochirality

One of life's most distinctive biochemical signatures is its strong selectivity for chiral molecular species, notably L-amino acids and D-sugars (Pasteur 1848; Bonner 1991; Nelson and Cox 2004). Most physical properties of enantiomeric pairs of molecules, including melting and boiling points, solubility, and intensive thermochemical properties, are identical. Consequently, unlike differential selection of amino acids onto quartz, prebiotic chiral molecular selection cannot be ascribed to net-charge effects. Instead, a confirmation-specific chiral environment must be invoked to explain any separation of left-handed from right-handed molecules.

Prebiotic synthesis processes generally yield equal amounts of L- and D-enantiomers (Lahav 1999; Mason 2000; Hazen 2005a). Thus, researchers have invoked two broad categories of symmetry-breaking phenomena to explain life's chiral excess (Bonner 1991, 1992, 1995; Pályi et al. 1999). Some authors claim that an important philosophical distinction exists between deterministic models of life's chirality (i.e., that some intrinsic feature of the universe inevitably leads to preferential selection of left-handed amino acids) vs. a chance local selection of left or right (i.e., life might have formed either way through local stochastic processes). Note, however, that of the many symmetry-breaking models proposed, parity violations (so-called "CP violations") in beta decay provide the only known universal chiral influence. Most authors conclude that this effect is so small as to be negligible in any realistic calculations of chiral selection (Bonner 1991, 1995).

All other proposed symmetry-breaking mechanisms are local, though at vastly different scales (i.e., Popa 1997). Some workers have favored nebular-scale processes such as chiral-selective photolysis by circular-polarized synchrotron radiation from neutron stars (Bailey et al. 1998; Clark 1999; Podlech 1999) or magnetochiral photochemistry (Rikken and Raupach 2000). These processes are consistent with the small but significant excess of L-amino acids reported from some carbonaceous chondrite meteorites (Engel and Macko 1997; Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Glavin and Dworkin 2006).

Other workers have focused on local "asymmetric agents"

(Avetisov et al. 1991; Popa 1997; Avetisov 1999). Some proposed mechanisms rely on local amplification of slight chiral excesses, for example by Bose-Einstein condensation (Chela-Flores 1994), or by chiral self-assembly of polymers (Bolli et al. 1997; Lippmann and Dix 1999; Saghatelian et al. 2001) or crystals (Eckert et al. 1993; Lahav and Leiserowitz 1999). However, the simpler, geochemically relevant chiral selection mechanism of adsorption on chiral mineral surfaces has been overlooked in large part (Lahav 1999; Jacoby 2002; Hazen and Sholl 2003).

Chiral mineral surfaces abound in the natural world. Quartz is the only common chiral rock-forming mineral (i.e., it occurs naturally in both left- and right-handed crystals), but all centric crystals also have the potential to display chiral fracture or growth surfaces (Hazen 2004; Downs and Hazen 2004), as well as chiral surface features such as steps and kink sites (Orme et al. 2001; Hazen and Sholl 2003; De Yoreo and Dove 2004). Common intrinsically chiral surfaces, in addition to those of quartz, include feldspar (110), clinopyroxene (110) and (111), olivine (111), clin amphibole (110) and (011), calcite (214), and gypsum (110) and (111) faces. Thus, selection and adsorption of organic molecules on mineral surfaces represents a viable mechanism for prebiotic molecular symmetry breaking.

It must be emphasized that left- and right-handed mineral surfaces are present on Earth in roughly equal abundance (e.g., Fronde 1978; Evgenii and Wolfram 2000), so it is natural to ask how a chiral bias in biochemical systems could arise. Advocates of mineral-induced handedness suggest that life's origin was a local molecular event, not dictated by global averages. A single successful self-replicating chiral synthesis, which assembled by chance on a left- or a right-handed crystal face, could dictate the dominant subsequent biochemical overprint in spite of initially racemic mixtures of both molecules and surfaces.

Minerals provide Earth's most chirally biased environments, and thus may represent the most likely loci for prebiotic chiral selection and amplification (Downs and Hazen 2004). Indeed, according to Lahav (1999), symmetry breaking by chiral surfaces offers a viable scenario for life's origin: "If a selective adsorption of chiral amino acids ... on certain crystal faces were observed, then the problem of biological homochirality would be possible to comprehend" (p. 259). In addition, synthesis and purification of chiral pharmaceuticals represents an industry with annual domestic sales approaching \$200 billion (Rouhi 2004). Given this importance to science and industry (e.g., Pályi et al. 1999; Jacoby 2002), new approaches to the selection and organization of chiral molecules warrant further study.

Chiral molecular selection by a crystal requires three, non-colinear interaction points between the molecule and mineral surface (e.g., Booth et al. 1996; Davankov 1997). Previous studies of adsorption of organic molecules on mineral surfaces have focused on symmetry-breaking effects of powdered right- vs. left-handed quartz, which is the most common acentric mineral (Bonner 1995; Soai et al. 1999). But, as noted above, all centric minerals also have the potential for symmetry breaking (McFadden et al. 1996; Sholl 1998; Lahav 1999; Attard 2001; Hazen et al. 2001, 2003; Hazen and Sholl 2003; Hazen 2004; Downs and Hazen 2004). Indeed, any general crystal face with a surface structure lacking a mirror or glide plane symmetry operator has the potential for chiral selectivity. This untapped potential for chi-

ral selectivity by common growth faces of rock-forming minerals represents a promising opportunity for further research.

Of fundamental importance to these chirality studies are measurements of interactions that occur on *specific* crystal faces, as opposed to bulk measurements on polycrystalline samples. Many aspects of mineral surfaces, including atomic structure (Hazen 2004; Downs and Hazen 2004), topographic features such as steps, kink sites, and etch pits (Joshi et al. 1970; Joshi and Paul 1977; Teng et al. 1998 and work in preparation; Orme et al. 2001; De Yoreo and Dove 2004), and electrochemical properties such as surface potential (Parsons 1990; Churchill et al. 2004), vary among the different crystallographic faces of a given crystal. Characterizations of these and other properties must be conducted on specific crystal faces if they are to be relevant to understanding stereoselective adsorption.

Consider chiral molecular selection on quartz (Tsuchida et al. 1935; Karagounis and Coumoulos 1938; Amariglio et al. 1968; Bonner et al. 1974, 1975; Soai et al. 1999). All of these studies employed powdered quartz crystals—a procedure that increases the reactive surface area but limits the possibility of determining the magnitude or identifying structural mechanisms of adsorption on *specific* surfaces. Different crystal growth faces of quartz display dramatically different adsorption characteristics, for example, in the differential formation of Fe-oxide coatings on the two symmetrically distinct rhombohedral faces, $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ (Fig. 2). The only effective way to study chiral adsorption, therefore, is to examine

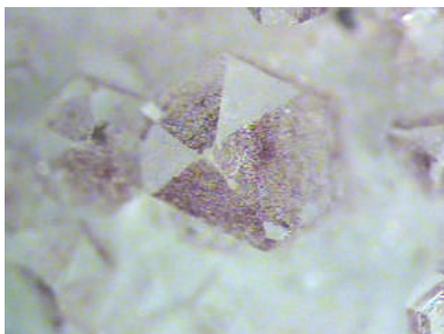
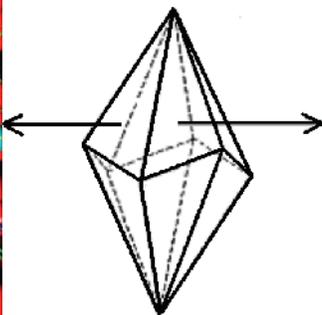
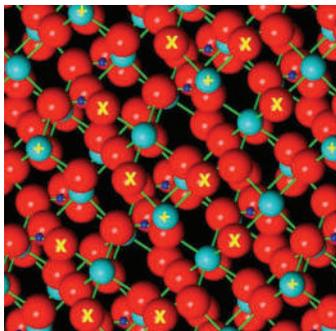


FIGURE 2. A quartz crystal (~1 mm diameter) displays selective deposition of Fe-oxide on $\{10\bar{1}1\}$ rhombohedral faces, compared to adjacent $\{01\bar{1}1\}$ rhombohedral faces. This behavior points to the possibility of differential, selective adsorption of molecular species on different quartz growth surfaces—a phenomenon not easily documented in powdered material. Photo by R.M. Hazen.



well-developed chiral growth faces on single crystals.

Accordingly, Hazen et al. (2001, 2003) demonstrated selective adsorption of D- and L- amino acids on calcite scalenohedral $\{214\}$ -type crystal faces, which are chiral. Calcite was chosen for several reasons that underscore the desirability of studying geochemically plausible origin scenarios: (1) calcite and other rhombohedral carbonate minerals were abundant in the Archean Era (e.g., Balley and Palmer 1989; Sumner 1997). (2) Calcite strongly adsorbs amino acids (Carter and Mitterer 1978; Lowenstam and Weiner 1989; Weiner and Addadi 1997; Alzenberg et al. 2001). (3) Calcite's surface growth topology is dramatically affected by adsorbed L- vs. D-amino acids (Teng and Dove 1997; Teng et al. 1998, 2000, and work in preparation; Orme et al. 2001; De Yoreo and Dove 2004). And (4) calcite's common $\{214\}$ -type scalenohedral crystal forms (Dana 1958), for example (214) and $(3\bar{1}4)$, have the potential for chiral selectivity (Fig. 3). [Note that all calcite Miller indices are here reported in terms of the hexagonal "structural unit cell" ($a = 5 \text{ \AA}$; $c = 17 \text{ \AA}$), which is the minimal unit cell determined by X-ray methods. These indices should not be confused with those of the hexagonal "morphological unit cell" ($a = 10 \text{ \AA}$; $c = 8.5 \text{ \AA}$), which has traditionally been used to describe calcite twinning, cleavage, and crystal forms (Dana 1958; Deer et al. 1971), or with either of two rhombohedral unit cells that further complicate the issue. Thus, for example, Miller indices for the cleavage face are (101) in the hexagonal morphological setting, but (104) in the preferred hexagonal structural setting.]

As a test of chiral selective adsorption, Hazen et al. (2001) immersed a calcite crystal in a racemic solution of aspartic acid. The crystal was rinsed in HPLC-grade water to remove excess amino acids, and any adsorbed amino acids from each individual face were then removed with HCl. Analyses of these acid washes demonstrated that "right-handed" (214) -type faces selectively adsorb D-aspartic acid, whereas enantiomeric (i.e., mirror-related) "left-handed" $(3\bar{1}4)$ -type faces selectively adsorb L-aspartic acid. However, similar experiments on calcite immersed in DL-alanine show no chiral selectivity (Hazen et al. 2003). These studies of calcite-amino acid interactions, which provide the first experimental demonstration of significant chiral molecular selectivity on growth surfaces of a centric mineral, point to the need for additional experiments.

Theoretical modeling of mineral-molecule chiral interactions

Theory provides an essential complement to experimental studies of mineral-molecule interactions. Integration of experi-

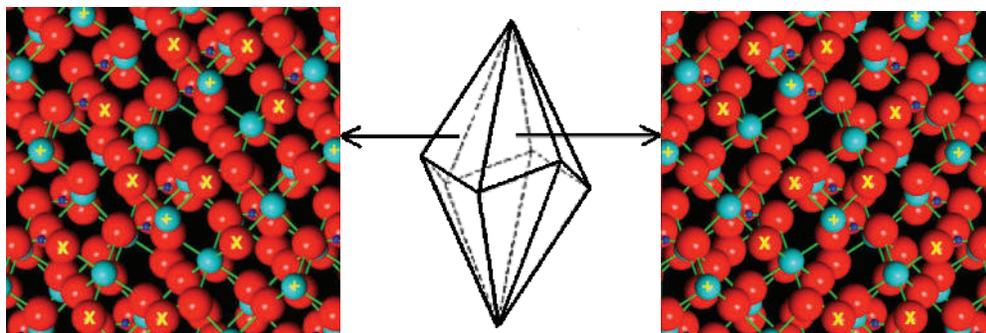


FIGURE 3. Adjacent crystal faces of calcite's common trigonal scalenohedral form have mirror-related surface structures (Hazen et al. 2001; Hazen 2004). Chiral surface structures of the $(3\bar{1}4)$ face (left) and the (214) face (right), which feature exposed O (X) and Ca (+) atoms, preferentially adsorb L- and D-aspartic acid, respectively.

ments and theoretical molecular methods has been carried out for (1) amino acids and carboxylic acids on metal and metal-oxide surfaces (Barbosa and Sautet 2001; Chen et al. 2002; Langel and Menken 2003; Toomes et al. 2003; Efstathiou and Woodruff 2003; Barlow and Raval 2003; Jones and Baddeley 2004); (2) anions adsorbed on oxide surfaces (Brown et al. 1998; Collins et al. 1999; Kubicki et al. 1999; Kwon and Kubicki 2004; Peacock and Sherman 2004; Yoon et al. 2004; Bargar et al. 2005; Persson and Axe 2005); and (3) aspartic acid on calcite (Orme et al. 2001; Kwon and Kubicki 2003). In addition, for the calcite-water interface, many theoretical simulations and observations exist to guide surface chemical models (Stipp and Hochella 1991; Van Cappellen et al. 1993; Hochella 1995; Vaughan 1995; de Leeuw and Parker 1997; Teng et al. 1998, 2000; de Leeuw et al. 1999; Fenter et al. 2000; Wright et al. 2001; Cygan et al. 2002; Stipp 2002; de Leeuw and Cooper 2004; Geissbuhler et al. 2004; Kristensen et al. 2004).

In the last decade, several authors have applied computational techniques to investigate chiral surfaces for their potential use in enantioselective synthesis and purification of chiral pharmaceuticals. The majority of these investigations have focused on chiral metal surfaces, which can be obtained by cutting a metal crystal along planes with high Miller indices and subsequent annealing (Sholl et al. 2001; Horvath and Gellman 2001; Asthagiri et al. 2002). This process yields surfaces with numerous steps and chiral kink sites, which act as the loci for chiral selection. Adsorption of chiral organic molecules on various chiral metal surfaces thus has been examined both experimentally and theoretically (McFadden et al. 1996; Sholl 1998; Ahmadi et al. 1999; Power and Sholl 1999; Attard 2001; Attard et al. 2002; Chen et al. 2002; Slijivancanin et al. 2002; Efstathiou and Woodruff 2003; Rankin and Sholl 2004). Temperature programmed desorption (TPD) studies of various chiral molecules on the chiral copper (643) surface have detected enantiospecific binding energies ranging from 0.06 to 0.25 kcal/mol (Horvath and Gellman 2001, 2002). Similar enantiospecific binding energies have been found in theoretical studies of physisorption of small chiral molecules on chiral surfaces of platinum and gold (Sholl 1998; Slijivancanin et al. 2002). An important conclusion of these studies is confirmation that an enantiospecific effect requires three non-colinear strong points of interaction with the chiral surface. Molecules with only two such interactions, by contrast, do not show significant chiral selectivity.

Theoretical modeling of mineral-molecule interactions, though computationally more intensive than metal-molecule or metal-water calculations, also provides an important complement to experiments. We wish to understand structural details of chiral bonded interactions between calcite and amino acids. For example, by what mechanism do right- and left-handed calcite {214}-type surfaces preferentially select D- or L-amino acids? Specifically, why are D- and L-aspartic acid more easily separated than D- and L-alanine? The chiral selection of aspartic acid on {214}-type faces implies a three-point interaction, in contrast to the non-chiral binding of alanine to calcite. What are the points of interaction? Accordingly, we have attempted to model the configuration of these mineral-molecule pairs using density functional theory (DFT) computational methods (Asthagiri et al. 2004; Asthagiri and Hazen 2004, and work in preparation).

As a first simplifying step, we have examined only the amino acid and the idealized flat mineral surface; water molecules are not included in our calculations. We thus assume that a direct and strong interaction exists between the amino acid and the mineral surface—an assumption supported by the presence of amino acids on calcite surfaces after vigorous washing treatments. In our experiments, we were able to recover adsorbed amino acids only after dissolution of the calcite surface by HCl. The final state of the mineral-molecule system certainly will be influenced by the aqueous system and its pH. Nevertheless, comparison of the relative binding energies and configurations of D- vs. L-amino acids on a given calcite surface provide insights regarding the structural basis for selective adsorption.

With optimized models of alanine and the calcite (214) surface, Asthagiri and Hazen (2004, and work in preparation) searched for minimum energy adsorption configurations (separately for D- and L-amino acids). Chiral selective adsorption is a function of the difference in energies of the two enantiomeric systems. We identified numerous local minima for both enantiomers of alanine on calcite (214) but found that the most stable minima for D- and L-alanine have negligible differences in adsorption energy (Fig. 4). Analyses revealed that there are only two strong interactions for alanine on calcite, as opposed to the three points required to obtain a chiral effect. The strongest interaction in the adsorbed system is between a Ca atom of the calcite surface and the O atom of alanine's carboxyl (COOH) group, while a secondary interaction occurs between a calcite surface O atom and a hydrogen of NH₂ (alanine's amino group). We conclude that the observed weak enantiospecificity results from the relative differences in dimensions of the alanine and the atoms on the calcite (214) surface: surface O and Ca atoms on calcite (214) are separated by 6 Å, whereas the separation of alanine NH₂ and COOH groups is roughly 4 Å. This dimensional disparity prevents the alanine molecule from forming three strong points of contact with the calcite surface, a prerequisite for strong enantiospecificity.

By contrast, we calculated a large enantiospecific effect for aspartic acid on the calcite (214) surface (Fig. 5), based on the formation of three strong mineral-molecule interactions. Aspartic acid features two carboxyl groups with an O-O separation similar to that of the calcite surface Ca-Ca separation. The two resultant Ca-O bonds between calcite and aspartic acid fix the orientation of the molecule on the mineral surface. In the case of D-aspartic acid, a third O-H bond readily forms between a calcite (214) surface oxygen and aspartic acid's amino group as a consequence of a fortuitously matching configuration. However, no such match is found for L-aspartic acid, which cannot form a third strong bond with the calcite (214) surface. Consequently, D-aspartic acid bonds preferentially to L-aspartic acid on calcite (214) surfaces by approximately 8 kcal/mol—the largest known chiral selective energy. This result is consistent with the experimental data of Hazen et al. (2001, 2003) and Orme et al. (2001) and shows the promise of using computational techniques to gain a better understanding of mineral-molecule interactions.

The real world

Real crystal surfaces are seldom flat. In the case of close-packed metal surfaces, including Pt, Ag, Au, and Cu, ideally

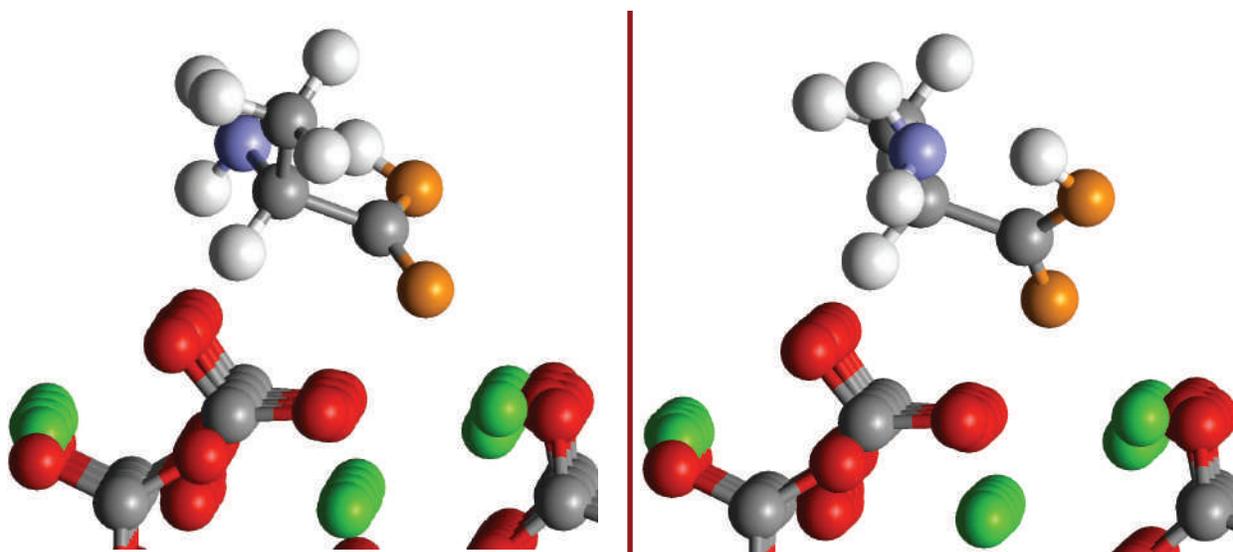


FIGURE 4. D-alanine (left) and L-alanine (right) bond to calcite (214) surfaces with two strong points of interaction—Ca from calcite bonds to O of the carboxyl group of alanine, and O from calcite bonds to the amino group from alanine. Calculations of Asthagiri et al. (2004) indicate that these two configurations have similar energies, consistent with experimental observations of no chiral selectivity (Hazen et al. 2003). The Ca, C, and O atoms of calcite are green, gray, and red, respectively; the C, N, O, and H atoms of alanine are gray, blue, orange, and white, respectively (from Asthagiri et al. 2004).

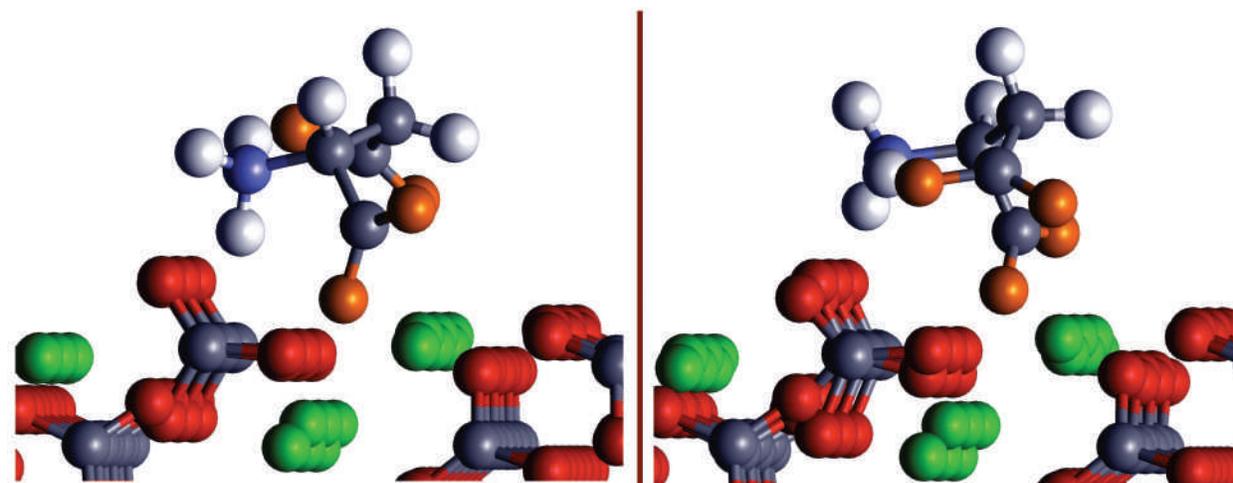


FIGURE 5. D-aspartic acid (left) bonds to calcite (214) surfaces with three strong points of interaction—two Ca atoms from calcite bond to O of the two carboxyl groups of aspartic acid, and O from calcite bonds to the amino group from aspartic acid. L-aspartic acid (right) forms only two strong bonds with this surface. Calculations of Asthagiri et al. (2004) indicate an enantiospecific energy of ~ 8 kcal/mol, consistent with experimental observations of chiral selectivity (Hazen et al. 2001). The Ca, C, and O atoms of calcite are green, gray, and red, respectively; the C, N, O, and H atoms of aspartic acid are gray, blue, orange, and white, respectively (from Asthagiri et al. 2004).

flat terraces can only exist for (100), (110), and (111). All other close-packed metal surfaces must incorporate steps and kinks. Chiral kink sites are thus intrinsic to all high-index surfaces and they dictate molecular adsorption behavior on these faces (McFadden et al. 1996; Sholl 1998; Power and Sholl 1999; Ahmadi et al. 1999; Gellman et al. 2001).

Mineral surfaces, with their lower symmetries and multiple crystallographically distinct atomic sites, present additional com-

plexities compared to metals. Although some common surfaces of rock-forming minerals can, in principle, be ideally planar at the atomic scale [e.g., quartz (100), graphite (001), and layer silicate (001)], most idealized surfaces are intrinsically irregular, such as the ~ 2 Å relief on the calcite (214) surface (Hazen 2004). Mineral surfaces also commonly incorporate growth defects, including step edges and kink sites, which provide promising docking loci for organic molecules (Orme et al. 2001; Hazen

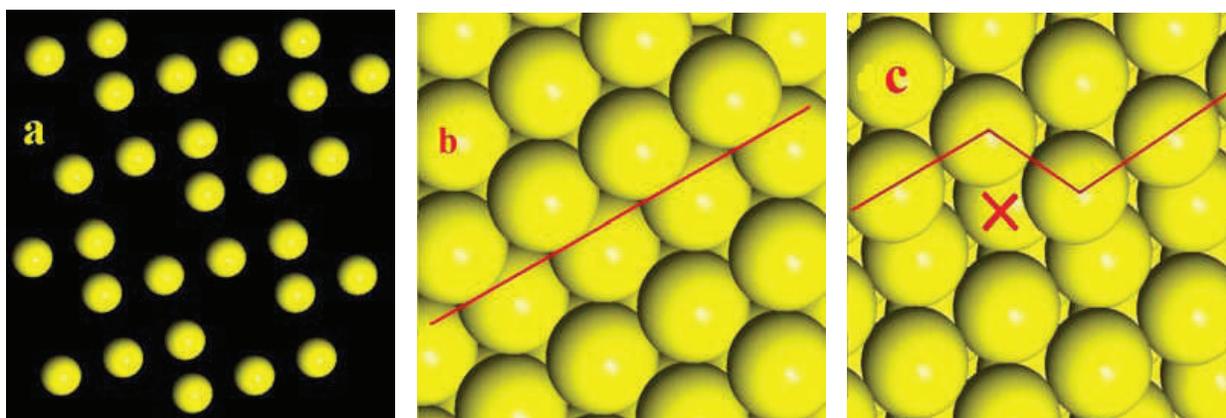


FIGURE 6. Crystals may incorporate three types of chiral surface features: (a) An idealized terrace, represented as a periodic two-dimensional chiral arrangement of atoms in a plane; these atoms may be coplanar or they may occur at slightly different heights. (b) A terrace step that is chiral along a step edge (red line). (c) A kink site that provides a chiral center (X). Experimental and theoretical studies (Sholl 1998; Orme et al. 2001; Hazen and Sholl 2003; De Yoreo and Dove 2004) reveal that molecular adsorption is enhanced at surface irregularities.

and Sholl 2003; De Yoreo and Dove 2004; see Fig. 6).

Of special note are the investigations of Dove and coworkers (Teng and Dove 1997; Teng et al. 1998, 2000; Orme et al. 2001; De Yoreo and Dove 2004; Elrahj et al. 2006), who have documented significant interactions between organic molecular species and calcite surface irregularities. Such interactions are strikingly revealed during crystal growth or dissolution in the presence of organic molecules, for example, of chiral amino acids. Asymmetric spiral growth edges and etch pits on the calcite (104) cleavage surface reveal that molecules preferentially dock along crystallographically distinct edges and kinks. Such binding may inhibit crystal growth in certain directions and thus result in unusual crystal morphologies (e.g., Cody and Cody 1991).

Mineral-molecule interactions may be highly specific to individual step edges, kink sites, and other irregularities. Teng et al. (in preparation), for example, observed that etch-pit morphologies on calcite (104) differ dramatically in the presence of different amino acids and carboxylic acids. Elhadj et al. (2006), furthermore, found

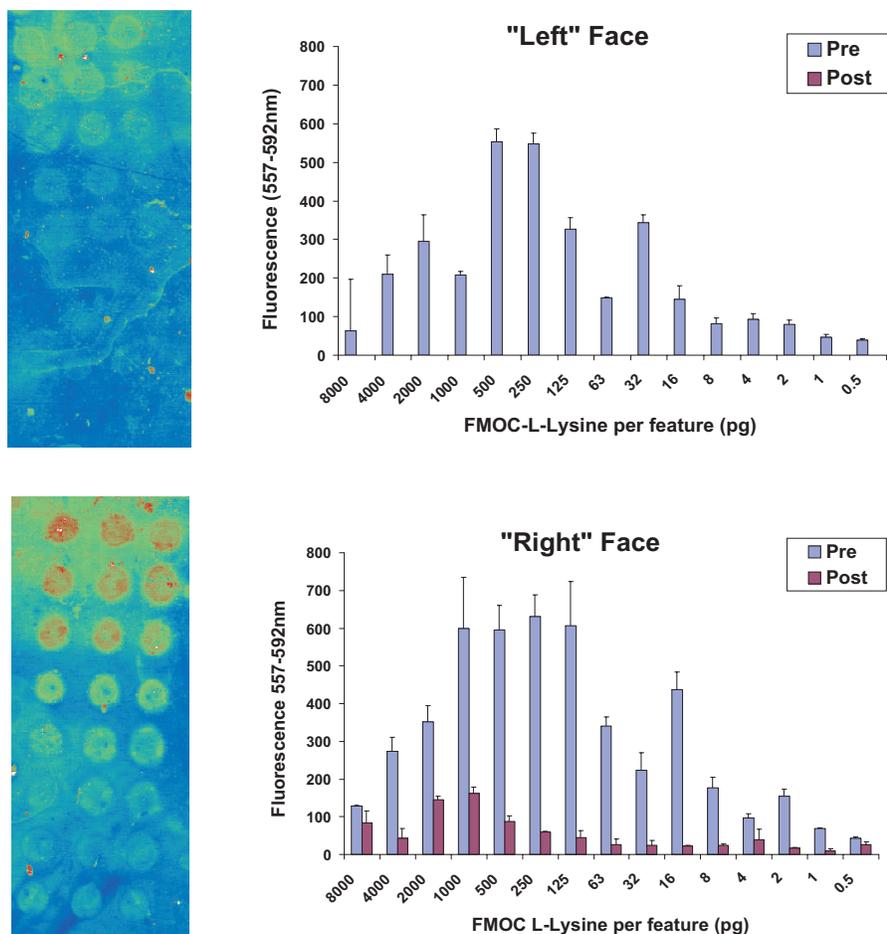


FIGURE 7. FMOc (i.e., fluorescent-tagged) L-lysine binds preferentially to (100) faces of right-handed quartz, compared to left-handed quartz. The images on the left show 1×3 mm areas of quartz crystals post-wash, with 3×8 arrays of $150 \mu\text{m}$ spots. Both quartz crystal faces were scanned at focal distance of maximum fluorescence signal (from Hazen et al 2004).

through experiments and modeling that polyaspartate (short peptide chains of aspartic acid molecules) demonstrate a cross-over from preferential binding on acute vs. obtuse step edges of calcite as the chain length increases from 1 to 6. Such exquisite molecular control on crystal orientation not only underscores the intricacies of modeling real-world prebiotic organic selection and organization, but also remains a key to understanding biomineralization and applications to nano-engineering (De Yoreo and Dove 2004). Given these complexities, we conclude that any realistic modeling of interactions between biomolecules and mineral surfaces must take into account three-dimensional geometries of both molecules and surfaces.

A problem of combinatorics

Experimental and theoretical studies provide useful insights regarding the interactions of specific mineral-molecule pairs. Nevertheless, the case-by-case investigation of interactions between hundreds of different naturally occurring mineral surfaces (including myriad possible three-dimensional surface irregularities) and thousands of plausible prebiotic molecules presents a daunting problem in combinatorics. To gain a useful overview of the problem, we need a rapid screening method to determine which molecules adhere to which surfaces.

Accordingly, Hazen et al. (2004, 2006) have modified DNA microarray techniques to study mineral-molecule interactions. Microarray technologies exploit microfluidic procedures to decorate solid surfaces with an array of ~ 100 μm diameter liquid dots. Originally designed for high throughput data mining of genomes, a microarray can accommodate $>10^6$ separate tests on a 2×4 cm surface (Sचना 2000). This technology thus is ideal for combinatoric screening of interactions between mineral surfaces and organic molecules (Holzwarth et al. 1998; Bunin et al. 1999; Korbel et al. 2001).

We have developed protocols for cleaning mineral surfaces, spotting the surfaces with up to 96 different organic molecular species, washing the surfaces to remove non-adsorbed molecules, and analyzing the adsorbed molecules. In trial experiments, we used a TeleChem Spotbot microarrayer to print 0.7 nL spots of Fmoc fluorescent labeled L-lysine onto left- and right-handed quartz (100) surfaces at eight different dilutions, each in triplicate to allow for surface variation. We scanned surfaces for fluorescence with a Genepix 4000B scanner, washed the surfaces with saline solution and then scanned again to observe preferential molecular binding post-wash (Fig. 7). We observed quantifiable preferential retention of Fmoc-tagged L-lysine on right-handed quartz (100) compared to that of left-handed quartz.

Standard microarray techniques find their principal applications in tagged DNA or peptide sequences and are thus limited to fluorescent or colored molecules (Udenfriend et al. 1972; de Bernardo et al. 1974; Cheng and Dovichi 1988; Kobayashi and Chiba 1994; Kang and Vanderhoek 1998; Korbel et al. 2001; Kahr and Gurney 2001; Sचना 2003). However, most plausible prebiotic molecules, including chiral amino acids, carboxylic acids, sugars, and lipids essential to life, are neither fluorescent nor colored. These species can be labeled with fluorescent tags, but such molecular tags will likely significantly alter adsorption behavior. Consequently, we have explored the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) as an analytical

tool to be coupled with microarray techniques (Vicenzi et al, work in preparation). ToF-SIMS is a reliable method for high-resolution detection and imaging of molecules (up to thousands of daltons) across a sample field (Benninghoven 1970; Briggs 1982; Vickerman et al. 1989). Each short pulse of primary ions emitted from a liquid Ga source produces a secondary ion mass spectrum via sputtering and mass separation in a drift tube. Only material from the uppermost molecular monolayers are desorbed and detected, thus making ToF-SIMS an extremely surface-sensitive technique. For example, recent studies have documented the surface detection of amino acids and pentose sugars adsorbed onto crystalline surfaces (Steele et al. 2001; Toporski and Steele 2004).

In a typical experiment, we arrayed 13 different molecular species (pentose sugars and amino acids) onto a $1 \times 1 \times 0.3$ cm (010) plate of albite. Each molecule was printed in triplicate at each of three dilutions (0.05, 0.5, and 1 M), thus yielding a 9×13 array (Fig. 8). Once an array is printed, ToF-SIMS analysis yields numerous spatially resolved mass fragments for each spot (Fig. 9). Pentose sugars, for example, produce characteristic $\text{C}_2\text{H}_3\text{O}$ fragments at 43.02 mass units, whereas amino acids produce characteristic $\text{C}_2\text{H}_5\text{N}$ fragments at 43.04 mass units. The intensity ratio of two such ion fragments, therefore, has the potential to indicate relative concentrations of different competing adsorbed molecular species. Furthermore, ratios of these molecular ion peaks to those of ion masses characteristic of the mineral surface (such as feldspar Si and Al ions) have the potential to reveal relative adsorption of different molecular species (Fig. 10).

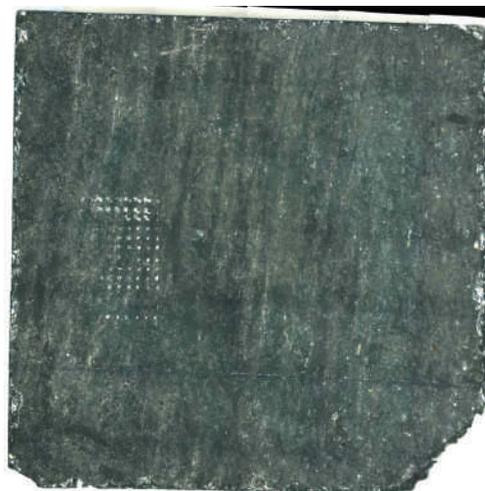


FIGURE 8. A pre-wash, reflected-light image of a 9×13 microarray on a 1×1 cm (010) plate of albite. Each row incorporates triplicate spots at three dilutions (0.05, 0.5, and 1 M). The 13 rows are: D-ribose, L-ribose, DL-ribose, D-arabinose, L-arabinose, DL-arabinose, D-lyxose, L-lyxose, DL-lyxose, D-xylose, D-lysine, L-lysine, and DL-lysine (from Hazen et al. 2006).

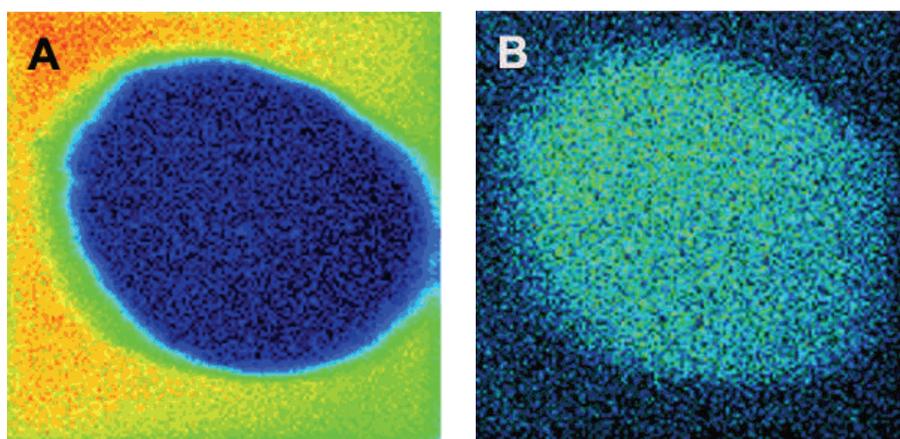


FIGURE 9. A single 150 μm array spot of lysine on calcite imaged with time-of-flight secondary ion mass spectrometry (ToF-SIMS). (a) Mass 42.96 ions from ^{43}Ca and ^{42}CaH (lysine masks the mineral surface so the spot appears dark). (b) Mass 43.04 $\text{C}_2\text{H}_5\text{N}$ amino acid fragment (from Hazen et al. 2006).

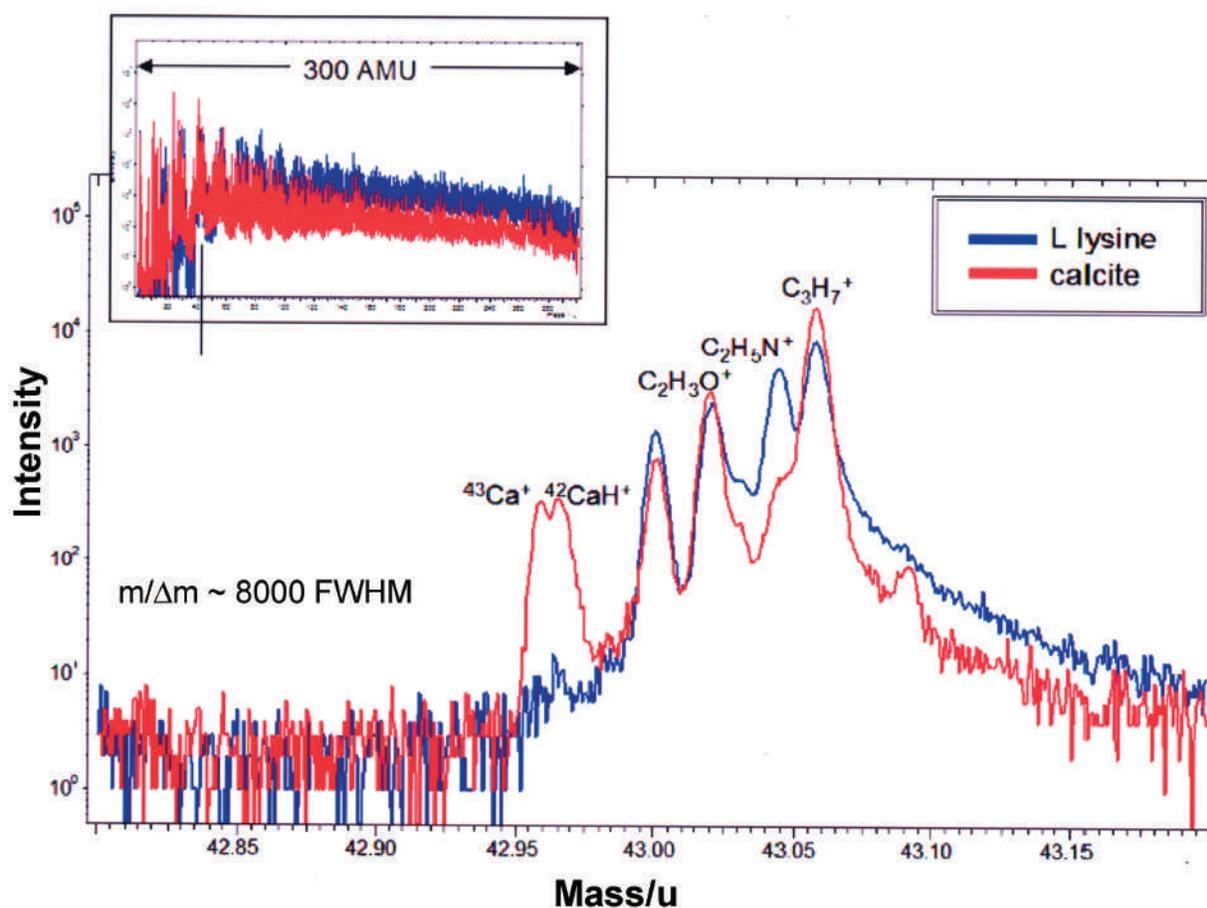


FIGURE 10. ToF-SIMS mass spectra (~ 43 mass units) of calcite (red) and lysine (blue). Calcite is distinguished by the 42.96 mass of ^{43}Ca and ^{42}CaH , whereas lysine is distinguished by the 42.04 mass of the $\text{C}_2\text{H}_5\text{N}$ fragment, which is typical of amino acids (from Hazen et al. 2006).

CONCLUDING REMARKS

Understanding prebiotic molecular selection and concentration presents a daunting problem in combinatorial chemistry. The Hadean Earth must have held a wealth of interesting organic species, as well as hundreds of different mineral surfaces possessing

a variety of atomic-scale surface features. Microarray technology coupled with ToF-SIMS analysis represents an efficient approach to probing numerous mineral-molecule interactions. Once a promising pair has been identified, an arsenal of additional experimental and theoretical approaches can be brought to bear in an effort to document structural details of these interactions.

Mineral-induced selection, concentration, and organization of prebiotic molecules into viable macromolecules represent key emergent steps in life's origins. These events set the stage for the emergence of self-replicating molecular assemblies (Rebek 1994; Kauffman 1993; Lee et al. 1996, 1997; Yao et al. 1998; Hazen 2005a) and the consequent triggering of molecular natural selection and evolution. The appearance of such a competitive, replicating, chemical system represents the defining transition from a geochemical to a biochemical world (Joyce 1994).

Our growing understanding of emergent complexity suggests that life's origin may not be a random, improbable event. Many emergent steps are hard-wired into the fabric of the Cosmos. Given hydrogen atoms, stars follow inevitably. Given stars, the periodic table of elements emerges, and from those elements come Earth-like planets. And many scientists are convinced that life is equally a cosmic imperative given a habitable world and sufficient time (de Duve 1995; Morowitz 2002).

The preceding naturalistic scenario for life's origins troubles many people. How can one believe in a benevolent God if life first emerged by an undirected sequence of chemical reactions? How can humans be created in God's image if evolution is an unscripted process of chance variations and competition?

Science can neither prove nor disprove the existence of God. Neither can science say whether or not the universe is imbued with meaning and purpose. But science remains our best hope of revealing the majesty of a Creation that is learning to know itself.

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