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Mineral Surfaces, Geochemical Complexities, and the Origins of Life

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Crystalline surfaces of common rock-forming minerals are likely to have played several important roles in life's geochemical origins. Transition metal sulfides and oxides promote a variety of organic reactions, including nitrogen reduction, hydroformylation, amination, and Fischer-Tropsch-type synthesis. Fine-grained clay minerals and hydroxides facilitate lipid self-organization and condensation polymerization reactions, notably of RNA monomers. Surfaces of common rock-forming oxides, silicates, and carbonates select and concentrate specific amino acids, sugars, and other molecular species, while potentially enhancing their thermal stabilities. Chiral surfaces of these minerals also have been shown to separate left- and right-handed molecules. Thus, mineral surfaces may have contributed centrally to the linked prebiotic problems of containment and organization by promoting the transition from a dilute prebiotic "soup" to highly ordered local domains of key biomolecules.

The question of life's origin is in essence a problem of information transfer from a geochemical environment to a highly localized volume. Earth's prebiotic environment possessed a varied inventory of raw materials—an atmosphere, oceans, rocks and minerals, and a diverse suite of small organic molecules. The processes by which the Hadean Earth was transformed to a living world required the selection, concentration, and organization of specific organic molecules into successively more information-rich localized assemblages. In this view, life's origins can be modeled as a problem in emergent chemical complexification (Morowitz 1992; de Duve 1995; Lahav 1999; Hazen 2005; Zaikowski and Friedrich 2007).

At least five aspects of Hadean geochemical environments contributed to Earth's prebiotic complexity and thus may have played significant roles in the emergence of life.

1. *Chemical Complexity*: The simplest chemical models for life's origins use only four essential elements—C, H, O, and N (e.g., Oparin 1938; Urey 1951; Morowitz 1992; Morowitz et al. 2000)—with the possible addition of S (Wächtershäuser 1990; de Duve 1995) and/or P (Westheimer 1987; Kornberg et al. 1999). Experiments to probe origins-of-life chemistry have often used correspondingly simple chemical systems (Miller 1953; Fox and Harada 1958; Oró 1961; Sanchez et al.

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1967; Shapiro 1988; Hennet et al. 1992; Marshall 1994; Eschenmoser 1999; Bernstein et al. 2002). Geochemical environments, in contrast, typically incorporate a dozen or more major and minor elements, with dozens more trace elements (Turekian 1968; Albarède and Hoffmann 2003; McSween et al. 2003; Steele et al. 2009). Therefore, it is important to consider the roles of a wider chemical spectrum in essential prebiotic reaction pathways.

2. *Interfaces*: Even given the most optimistic assessments of exogenous and endogenous sources of prebiotic organic molecules (Chyba and Sagan 1992), the Hadean oceans or large terrestrial bodies of water would have been extremely dilute (Pinto et al. 1980; Stribling and Miller 1987; Cohn et al. 2001). Mechanisms for the selection and concentration of essential biomolecules are thus required. In this regard, numerous authors have focused on the effectiveness of interfaces between minerals and aqueous solutions (Goldschmidt 1952; Cairns-Smith and Hartman 1986; Lahav 1994; Ertem and Ferris 1996; Ferris 1999, 2005; Ertem 2002; Schoonen et al. 2004; Hazen 2006), or among immiscible fluids (Lasaga et al. 1971; Deamer and Pashley 1989; Morowitz 1992; Dobson et al. 2000; Tuck 2002; Monnard et al. 2002). Such surfaces provide loci where organic molecules can be selected and concentrated from more dilute solutions.

3. *Gradients*: Gradients were important disequilibrium features of the Hadean Earth. Thermal gradients were sustained both by solar radiation and by geothermal heat, whereas chemical gradients were produced by mineral dissolution and the mixing of different fluid reservoirs. Thermal and chemical gradients are striking characteristics of hydrothermal systems, both on the deep ocean floor and in near-surface continental environments. At modern-day deep sea hydrothermal vents, for example, thermal gradients may reach 300°C at scales of a few centimeters, whereas significant gradients in pH, oxidation state, and in dissolved cationic and anionic species occur at scales significantly less than a meter (Shock 1992; Carl 1995; Van Dover 2000; Kelley et al. 2005). Less severe gradients also occur at off-axis hydrothermal systems, and during mixing of fluids of differing salinities, for example where river waters enter the oceans.

4. *Fluxes*: The dynamic circulation and mixing of fluids through such varied processes as hydrothermal venting, ocean currents, stream and groundwater flow, winds, and tides is another ubiquitous disequilibrium feature of Earth's near-surface environment.

5. *Cycles*: The prebiotic geochemical characteristics perhaps most critical for life's origins were pervasive cycling of environmental conditions at or near Earth's Hadean surface. Periodic cycles such as day-night, high tide-low tide, hot-cold, and wet-dry subjected prebiotic chemicals to repeated selective pressures and thus winnowed the pool of available chemical species. Episodic events, including asteroid impacts and volcanic eruptions, added additional selective pressures to the near-surface organic inventory.

These five geochemical characteristics must be considered individually and collectively in origins-of-life models. This article focuses primarily on just one of these aspects, the possible roles of crystalline surfaces of common rock-forming minerals, which provided ubiquitous crystal-fluid interfaces for a variety of molecular processes. The mineral-water interface is a dynamic, energetic environment that can selectively adsorb biomolecules, increase the thermal stability of organic species, promote chemical reactions, and facilitate the type of molecular concentration and organization that must have preceded life's origins.

BACKGROUND

Chemical interactions at crystal-water interfaces are crucial to a wide range of scientific and technological topics, including corrosion, heterogeneous catalysts, chemical sensors, teeth and bones, titanium implants and other prosthetic medical devices, and myriad commercial products including paints, glues, dyes, lubricants, solvents, and cleaners. Geochemists pay special attention to reactions between mineral surfaces and aqueous species—interactions central to weathering, soil formation, hydrothermal ore-forming fluids, biomineralization, biofilm formation, uptake and release of chemicals that affect water quality, and many other natural processes (Davis and Kent 1990; Stumm 1992; Vaughan 1995; Hochella 1995; Drever 1997; Langmuir 1997; Brown et al. 1998; Brown and Parks 2001; Davis et al. 2004; De Yoreo and Dove 2004; Lee et al. 2006, 2007; Glamoclija et al. 2009). Studies of mineral-molecule interactions related to origins of life build on this vast geochemical literature.

On the Nature of Mineral Surfaces

The idealized crystalline surface terminates in an arrangement of atoms that approximates the planar truncation of a periodic three-dimensional crystal structure (Fig. 1A). In real crystals this ideal situation is altered in several ways (e.g., Hochella and White 1990; Somorjai 1994; Hochella 1995; Vaughan 1995; Brown et al. 1998). First, surface atoms reside in an environment quite different from those below the surface, and thus undergo relaxation owing to boundary effects—typically slight deviations from their formal crystallographic positions (Hochella 1990; Stipp and Hochella 1991; Wright et al. 2001). Second, mineral surfaces in air or an aqueous medium are commonly subject to chemical alteration through oxidation, hydration, or hydroxylation (Guevremont et al. 1998; Biino et al. 1999; Stipp 2002). Third, crystals invariably have defects and impurities that alter local surface physical properties and chemical reactivity (Hochella 1990; Cygan et al. 2002).

The topology of real crystal surfaces also represents an important deviation from ideality because crystal surfaces are seldom flat. In the intensively studied case of cubic close-packed metal surfaces, including Pt, Ag, Au, and Cu, ideally flat terraces can only exist for (100), (110), and (111). All other surfaces of these metals must incorporate steps and/or kinks (Fig. 1B and C). Kink sites are intrinsic to all high-index surfaces, whether on metals or minerals, 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 complexities compared with metals (Lasaga 1990; Hazen 2004). Although some common surfaces of rock-forming minerals can be ideally planar at the atomic scale (e.g., the [100] plane of quartz [SiO_2], the [001] planes of graphite [C] and molybdenite [MoS_2], and the [001] planes of varied layer silicates such as micas and

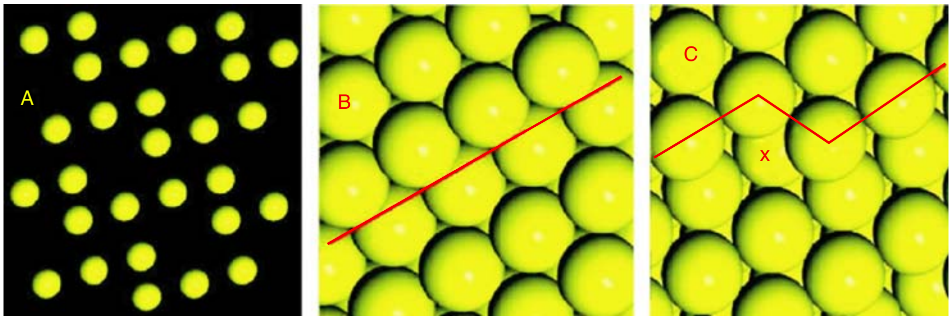

Figure 1. Crystal surfaces display a variety of atomic surface features. (*A*) The surface of an ideal crystal may be represented as a periodic two-dimensional arrangement of atoms; these atoms may be coplanar or they may occur at slightly different heights. Real crystals feature surfaces that are typically stepped (*B*) or kinked (*C*). Kink sites provide chiral (left- or right-handed) centers (X). Experimental and theoretical studies reveal that molecular adsorption is enhanced at such surface irregularities.

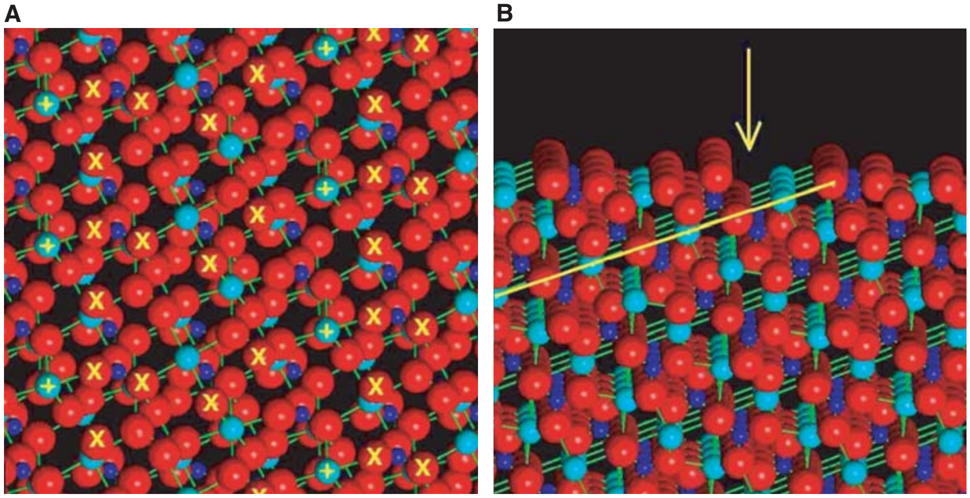

Figure 2. The common calcite form of $CaCO_3$ often displays chiral surfaces. (*A*) The structure of the (21–34) face of calcite features a chiral arrangement of positive (+) and negative (X) charge centers near the crystal termination. Ca, C, and O atoms are turquoise, blue, and red, respectively. In this 20 × 20 Å view the (01–8) axis is vertical—an orientation that provides a useful image of the surface structure. (*B*) A view of this surface tilted 3° from horizontal (projected almost down the [01–8] axis) reveals the irregular surface topology, including 2-Å-deep steps (yellow arrow) that result from the oblique intersection of layers of Ca and rigid CO_3 groups with the surface (yellow line).

chlorites), most surfaces are intrinsically irregular, as shown by the ~2 Å relief on the common (21–34) surfaces of calcite ($CaCO_3$) (Fig. 2) (Hazen 2004). Mineral surfaces also commonly incorporate growth defects, including step edges and kink sites, which provide promising docking loci for organic molecules (Lasaga 1990; Teng and Dove 1997; Teng et al. 1998; Orme et al. 2001; Hazen and Sholl 2003; De Yoreo and Dove 2004). For example, Teng et al. (2006) showed the step-dependent adsorption of succinic acid (1,4-dicaboxlyic acid) on irregular (10–14) growth surfaces of calcite. The presence of succinic acid in solution blocks certain growth directions and thus dramatically modifies calcite surface growth morphology.

Additional complexities arise from a variety of geological materials that do not have periodic two-dimensional surfaces, notably amorphous materials such as basaltic glass from seafloor volcanoes. Mesoporous zeolites and nanoparticulate clays (including layer phyllosilicates and hydroxide minerals) interact with organic molecules in complex three-dimensional environments (Smith 1998; Greenwell and Coveney 2006; Benetoli et al. 2007). For example, Pitsch et al. (1995) showed that double-layer hydroxide minerals such as hydrotalcite efficiently adsorb glycoaldehyde phosphate and formaldehyde, presumably into their relatively spacious inter-layer regions, and promote condensation reactions to tetrose and hexose sugar phosphates. Given these complexities, any realistic modeling of interactions between biomolecules and mineral surfaces must take into account the geometries of both molecules and surfaces.

On the Nature of the Mineral–Water Interface

Mineral surfaces undergo significant modifications in an aqueous environment, especially in an electrolyte solution such as sea water (Parks 1990; Davis and Kent 1990; Van Cappellen et al. 1993; de Leeuw and Parker 1997; de Leeuw et al. 1999; Wright et al. 2001; Stipp 2002). In the classic electrical double layer (EDL) model, a crystal surface in pure water directly contacts a compact quasi-periodic layer of H^+ or OH^- ions, whereas a second diffuse layer of mobile ions extends from the compact layer a few Ångstroms into the fluid. The nature of the

EDL is strongly dependent on pH: At lower pH, the surface is typically protonated and thus positively charged, whereas at higher pH, the surface is negatively charged with hydroxyls. The crossover pH at which the surface is electrically neutral is called the point of zero charge (pH_{PZC}).

It is important to recognize that crystallographically distinct faces on the same crystal will have different surface structures, and thus may have significantly different pH_{PZC}s, surface reactivities, and other properties (Guevremont et al. 1998; Hung et al. 2003; Churchill et al. 2004). For this reason, powdering a crystal sample to increase the reactive surface area in an experiment may destroy significant information regarding specific reaction mechanisms associated with specific crystallographic faces (Hazen 2006).

On the Nature of Mineral–Molecule Interactions

Adsorbed ionic and molecular species modify the electrical double layer of mineral surfaces by displacing OH^-, H^+, and H_2O at the solid-fluid interface. Recent developments in surface complexation modeling enable accurate modeling of surface speciation. Sverjensky and Fukushi (2006) developed an extended triple-layer (ETL) model to account for the process of inner-sphere surface complexation by ligand exchange. The ETL model treats a previously neglected phenomenon integral to ligand exchange reactions: the electrostatic work during desorption of water dipoles from a charged surface. The magnitude of this work is substantial and depends only on the stoichiometry of the surface reaction. When structures of adsorbed anions established in spectroscopic studies are used to calibrate an ETL model of bulk adsorption data, the model can independently predict proportions of inner- to outer-sphere surface complexes as functions of pH, ionic strength, and surface coverage—proportions that have been confirmed in experiments, for example in studies of aspartate and glutamate adsorption on titanium dioxide (e.g., Jonsson et al. 2009).

More than a century of experimental and theoretical research has explored the interaction of dissolved aqueous chemical species with mineral surfaces (for reviews see, e.g., Parsons 1990; Hochella and White 1990; Brown et al. 1998). Most of this extensive literature focuses on dissolved ions and inorganic complexes; however, many of the principles developed for mineral–ion interactions also apply to biomolecules.

All surface-promoted reactions require at least one molecular species to interact with the surface. These interactions can be mediated by water molecules, protons, or hydroxyl groups through relatively weak interactions (outer-sphere adsorption, or "physisorption"). Alternatively, one or more chemical bonds can form (inner-sphere adsorption, or "chemisorption"). Chemisorbed ions typically bond to one or two surface atoms, whereas larger molecules can adopt a variety of surface topologies with multiple attachments (Fig. 3), as discussed later in this article (Davis and Kent 1990; Zhang et al. 2004; Sverjensky et al. 2008; Jonsson et al. 2009).

Details of molecular adsorption are dependent on several variables, most notably pH, the nature and concentrations of molecular solutes, and the identities and concentrations of electrolytes (Schindler 1990; Sverjensky 2005; Sverjensky and Fukushi 2006; Jonsson et al. 2009). Additional complexities arise when organic molecules interact with crystal surface irregularities (Teng and Dove 1997; Teng et al. 1998, 2000; Orme et al. 2001; De Yoreo and Dove 2004; Elhadj et al. 2006). Such interactions can be strikingly revealed during crystal growth or dissolution in the presence of organic molecules, which can 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., Teng et al. 2006). For example, Cody and Cody (1991) showed strikingly varied skewed growth of macroscopic gypsum ($CaSO^4H_2O$) crystals in the presence of 28 different chiral organic solutes, including amino acids and carboxylic acids. Such exquisite molecular control of crystal growth and orientation points to strategies for nano-engineering and underscores the intricacies of modeling real-world prebiotic organic selection and organization (De Yoreo and Dove 2004).

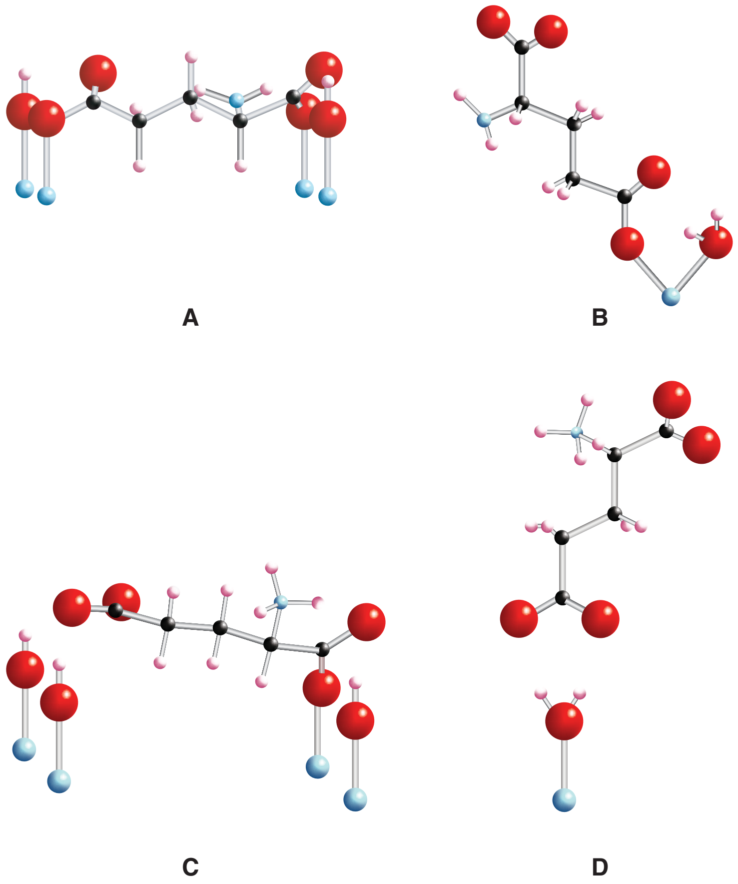

Figure 3. Amino acids bind in different ways to mineral surfaces. Numerous possible modes of attachment exist for glutamate adsorbed to rutile (TiO_2) surface sites, consistent with surface complexation calculations (Sverjensky et al. 2008; Jonsson et al. 2009). Large red spheres indicate oxygen atoms, small black spheres carbon, small pink or blue spheres hydrogen or nitrogen, respectively, and the lowermost blue spheres titanium at the rutile surface. (*A*) Bridging-bidentate species with four points of attachment involving one inner-sphere Ti-O-C bond and one Ti-OH. . .O=C hydrogen bond for each carboxylate. (*B*) Chelating species with two points of attachment involving one inner-sphere Ti-O-C bond and one Ti-OH_2^+. . .O=C to a single titanium. (*C*) Alternative to the bridging-bidentate species in (*A*). This bridging-bidentate species has four points of attachment involving one inner-sphere Ti-O-C bond and one Ti-OH. . .O=C hydrogen bond of the a-carboxylate, and one Ti-OH. . .$^-$O-C hydrogen bond and one Ti-OH. . .O=C hydrogen bond of the g-carboxylate (stabilized through resonance). (*D*) Alternative to the chelating species in (*B*), outer-sphere or hydrogen bonded to the surface. After Jonsson et al. 2009.

Mineral Evolution

Any consideration of minerals and the origins of life must take into account which mineral species were available on the Hadean Earth. Recent studies have shown that the diversity and distribution of minerals at or near Earth's surface has changed dramatically over geological time (Hazen et al. 2008). Perhaps two-thirds of the approximately 4400 known mineral species represent weathering products owing to a biologically oxidized atmosphere, and thus are the indirect consequence of life. The nature and abundances of hydroxides, zeolites, and clay minerals, which are often invoked in origins-of-life models, were undoubtedly very different from today (Schoonen et al. 2004; Hazen et al. 2008). Many other minerals that concentrate rare pegmatophile elements such as Li, Be, Cs, Ta, and U may have taken a billion years or more to form, and so their first appearances would have postdated the origins of life (Grew and Hazen 2009; Hazen et al. 2009). Thus, origin-of-life scenarios that invoke rare or exotic minerals such as uraninite (UO_2) (Adam 2007) or colemanite $[Ca_2B_6O_{11}{\cdot}5(H_2O)]$ (Ricardo et al. 2004) may be untenable.

RECENT RESULTS

The first emergent step in life's origin, the prebiotic synthesis of biomolecules, is also the best understood. Since the pioneering synthesis studies of Stanley Miller and Harold Urey (Miller 1953; Miller and Urey 1959; see also Wills and Bada 2000), facile production of organic molecules has been shown for several plausible prebiotic environments (Chyba and Sagan 1992; Lahav 1999; Fry 2000; Hazen 2005). 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, for example, the problem of amino acids. More than 70 different amino acids have been extracted from the Murchison meteorite and other carbonaceous chondrites (Cronin and Chang 1993; Sephton 2002; Pizzarello and Weber 2004; Pizzarello 2006; Martins 2007). This inventory, moreover, contains a mixture of both left- and right-handed amino acids, although by some accounts concentration of L-amino acids exceeds D-amino acids in some meteorites (Pizzarello and Cronin 2000; Pizzarello 2006). Life, in contrast, uses 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 show similar molecular selectivity (Nelson and Cox 2004; Hazen 2005). 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 (Bernal 1951; Goldschmidt 1952; Lahav 1994). The following sections thus consider recent results on aspects of mineral-mediated molecular synthesis, selection, and organization.

Mineral-"Catalyzed" Organic Synthesis

The synthesis of small organic molecules from inorganic precursors, including mineral-mediated synthesis, is perhaps the best understood aspect of life's origins. For example, recent experiments by several groups have shown production of ammonia from reactions of N_2 or nitrate with a wide range of oxides or sulfides (Brandes et al. 1998, 2008; Schoonen and Xu 2001; Dorr et al. 2003); thiols from CO_2 and sulfides (Heinen and Lauwers 1996); and amino acids and other compounds from CO or CO_2, NH_3, and H_2O and sulfides (Nakajima et al. 1975; Huber and Wächtershäuser 1997, 2006; Schoonen et al. 1999; Cody et al. 2000, 2001, 2004). Transition metal oxide or sulfide minerals are not true catalysts in these reactions because the surface is altered; rather, the minerals participate as reactants through a redox couple, for example:

$$CO_2 + FeS + H_2S \rightarrow HCOOH + FeS_2 + H_2O \; (e.g., \text{Cody2004}), \text{or}$$

$$4Cu_2O + 2H_2O + NO_3^- \rightarrow NH_3 + 8CuO + OH^- \; (\text{Brandes et al. 2008}).$$

Alternatively, many common minerals have been shown to catalyze carbon addition reactions, including Fischer-Tropsch-type synthesis and hydroformylation (Heinen and Lauwers 1996; McCollum et al. 1999; Cody et al. 2004). Varied roles of minerals in the synthesis of small organic molecules have been reviewed recently by Cody (2004) and Schoonen et al. (2004) and are not considered further here.

Molecular Adsorption and Stabilization

Experimental and theoretical investigations have documented the nature of molecular adsorption for numerous mineral-molecule combinations (e.g., Lambert 2008; Lambert et al. 2009). Dozens of recent studies reveal complexity in structure and speciation of adsorbed organics, particularly through in situ FTIR and other spectroscopic studies (Somasundaran and Krishnakumar 1994; Rodriguez et al. 1996; Holmen et al. 1997; Roddick-Lanzilotta et al. 1998; Fitts et al. 1999; Klug and Forsling 1999; Kubicki et al. 1999; Roddick-Lanzilotta and McQuillan 1999, 2000; Duckworth and Martin 2001; Sheals et al. 2002; Lackovic et al. 2003; Rosenqvist et al. 2003; Yoon et al. 2004, 2005; Johnson et al. 2004a, 2004b, 2004c, 2005a, 2005b; Trout and Kubicki 2004; Persson and Axe 2005; Perezgasga et al. 2005; Benetoli et al. 2007; Arora and Kamaluddin 2009; Kitadai et al. 2009; Pászti and Guczi 2009). Important conclusions of these studies include the recognition of multiple adsorption configurations, including both single and multiple inner- and outer-sphere binding, for a given mineral-molecule pair.

Integration of experiments and theoretical molecular methods has been performed for amino acids on metal surfaces (Chen et al. 2002; Toomes et al. 2003; Efstathiou and Woodruff 2003; Barlow and Raval 2003; Jones and Baddeley 2004), for anions adsorbed on oxide surfaces (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 for varied biomolecules on calcite (Thomas et al. 1993; Orme et al. 2001; Asthagiri and Hazen 2007). In addition, for the calcite-water interface, many theoretical simulations and observations exist to guide surface chemical models (Stipp and Hochella 1991; de Leeuw and Parker 1997, 1999; Teng et al. 1998, 2000; Fenter et al. 2000; Wright et al. 2001; Stipp 2002; de Leeuw and Cooper 2004; Geissbuhler et al. 2004; Kristensen et al. 2004).

Recent studies of organic anion adsorption on oxide surfaces show complex surface speciation: both inner- and outer-sphere species vary in relative importance over a range of pH, ionic strength, and surface coverage. Many investigations document significant variations in proportions of inner- to outer-sphere species as a function of pH or surface coverage (e.g., Hug and Sulzberger 1994; Fitts et al. 1999; Nowack and Stone 1999; Roddick-Lanzilotta and McQuillan 2000; Lackovic et al. 2003; Sheals et al. 2003; Persson and Axe 2005). Proton titrations of oxide surfaces in electrolyte solutions, both with and without an organic adsorbate, provide powerful constraints on the possible reactions responsible for adsorption, particularly when used in combination with in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) studies (Holman and Casey 1996; Nordin et al. 1997; Boily et al. 2000a, 2000b, 2000c, 2005; Sheals et al. 2002, 2003; Lackovic et al. 2003; Lindegren et al. 2005). However, with few exceptions (Gisler 1981; Whitehead 2003; Vlasova and Golovkova 2004; Vlasova 2005; Jonsson et al. 2009). Most adsorption studies of amino acids on oxide surfaces have been limited to systems without control of pH and ionic strength (e.g., Holm et al. 1983; Matrajt and Blanot 2004).

The work of Jonsson et al. (2009, 2010), who studied the adsorption of L-glutamate and L-aspartate on the surface of rutile (α-TiO$_2$, pH$_{\mathrm{PZC}} = 5.4$) in NaCl solutions using potentiometric titrations and batch adsorption experiments over a wide range of pH, ligand-to-solid ratio, and ionic strength, illustrates the need for such integrated studies. Not only did they find that adsorption depends strongly on ionic strength and glutamate concentration, but the extended triple-layer surface complexation model of all the experimental results also indicated the existence of at least two surface glutamate complexes. For example, one possible mode of glutamate attachment involves a bridging-bidentate species binding through both carboxyl groups, which can be thought of as "lying down" on the surface (as found previously for amorphous titanium dioxide and hydrous ferric oxide) (Fig. 3A). Another adsorption mode involves a chelating species, which binds only through the γ-carboxyl group, i.e., "standing up" at the surface (Fig. 3B). The calculated proportions of these two surface glutamate species vary strongly, particularly with pH and glutamate concentration (Fig. 4). Any model of prebiotic interactions between mineral surfaces

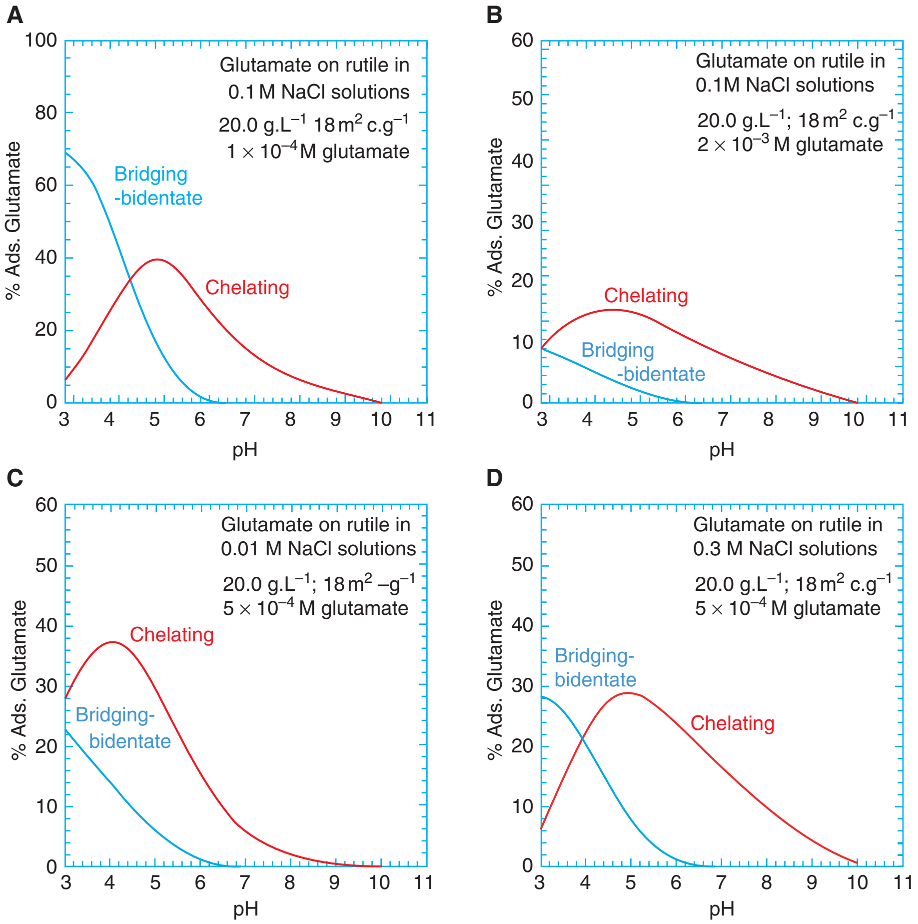

Figure 4. Predicted surface speciation of glutamate on rutile as a function of environmental conditions. The species names refer to the pictures in Figure 3. After Jonsson et al. 2009.

and biomolecules must take these added complexities into account.

Chiral Molecular Adsorption

A key attribute of life, and an important consideration in origins-of-life models, is life's molecular handedness, or chirality. Chiral crystalline surfaces provide effective environments for discrimination of left- and right-handed molecules in both natural and industrial contexts (Hazen and Sholl 2003). A chiral crystal surface is defined as any terminal arrangement of atoms that cannot be superimposed on its reflection in a mirror perpendicular to the surface. Such surfaces have long been cited in reference to their possible role in the origins of biochemical homochirality (Tsuchida et al. 1935; Karagounis and Coumoulos 1938; Amariglio et al. 1968; Bonner et al. 1975; Lahav 1999; Hazen et al. 2001). More recently, these crystal surfaces have received attention for their potential applications in the selection and purification of chiral pharmaceuticals and other molecular products (Soai et al. 1999; Kahr and Gurney 2001; Jacoby 2002; Rouhi 2004).

Most studies have focused on the behavior of chiral surfaces of cubic close-packed (CCP) metals, including copper, silver, gold, and platinum. Theoretical studies of these metal surfaces have shown the potential for significant differences in adsorption energies of right- versus left-handed molecules (McFadden et al. 1996; Sholl 1998; Šljivančanin et al. 2002), whereas experiments provide indirect evidence for chiral selectivity (Ahmadi et al. 1999; Attard 2001; Sholl et al. 2001; Horvath and Gellman 2001, 2002; Kühnle et al. 2002). Less attention has been devoted to the wide variety of chiral oxide and silicate mineral surfaces, which are ubiquitous in Earth's crust. Such surfaces provide the most abundant and accessible local chiral geochemical environments, and thus represent logical sites for the prebiotic chiral selection and organization of essential biomolecules (Hazen and Sholl 2003; Hazen 2004, 2005, 2006; Castro-Puyana et al. 2008). Hazen et al. (2001) first showed chiral-selective mineral adsorption, specifically of aspartate on the common (21–34) surfaces of calcite ($CaCO_3$), whereas alanine displayed no such selection. Subsequent calculations (Asthagiri et al. 2004; Hazen 2006; Asthagiri and Hazen 2007) rationalize these results by demonstrating that aspartate, but not alanine, binds to the calcite surface with three noncolinear attachments (Fig. 5)—a prerequisite for chiral selection (Davankov 1997).

Numerous other common rock-forming minerals, including quartz (SiO_2), alkali feldspar [$(Na,K)AlSi_3O_8$], and clinopyroxene [$(Ca,Mg,Fe)SiO_3$], possess chiral crystal surfaces (Hazen 2004). One or more of these minerals is present in most rocks in Earth's crust, as well as on the Moon, Mars, and other terrestrial bodies, so chiral crystal environments are correspondingly ubiquitous. Furthermore, any irregular mineral fracture surface will provide an additional variety of local chiral environments. These natural chiral surface environments occur in both left- and right-handed variants in approximately equal proportions (Frondel 1978; Evgenii and Wolfram 1978). Nevertheless, the widespread occurrence of local chiral environments provided the prebiotic Earth with innumerable sites for experiments in chiral selection and organization—experiments that may have led, through a process of chiral amplification, to a fortuitous, self-replicating homochiral entity (Bonner 1991, 1995; Lippmann and Dix 1999; Zepik et al. 2002; Klussman et al. 2006, 2007; Noorduin et al. 2008).

Mineral-induced Polymerization

Many of life's essential macromolecules, including proteins, carbohydrates, and DNA, form from water-soluble monomeric units—amino acids, sugars, and nucleic acids, respectively. Under some (but not all) conditions, these polymers tend to break down rather than form in an aqueous medium (Shock 1993). Mineral surfaces provide a means to concentrate and assemble these bio-monomers. Lahav et al. (1978) showed 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

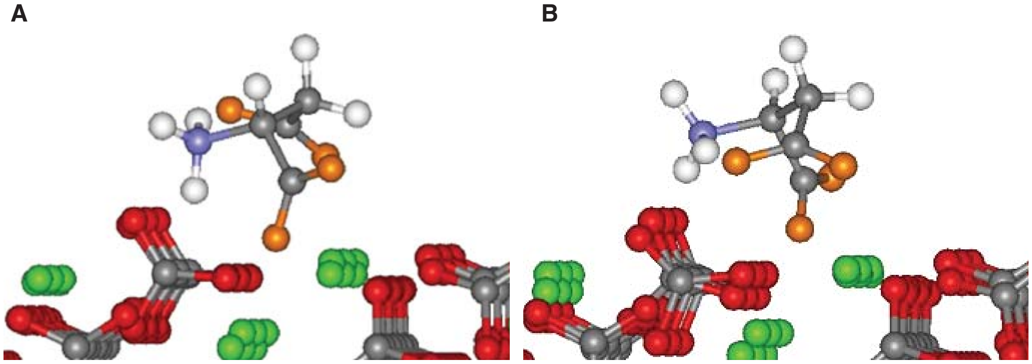

Figure 5. The most stable configurations for L- and D-aspartate on the calcite (21–34) surface (*A* and *B*, respectively). The D enantiomer, which requires significantly less calcite surface relaxation and aspartate distortion, is favored by 8 Kcal/mol—the largest known enantiospecific effect.

the presence of clays—a situation not unlike the evaporation that might have repeatedly dried up shallow prebiotic ponds or tidal pools. Numerous subsequent studies have elucidated the adsorption and polymerization of amino acids on varied crystalline surfaces (Zamaraev et al. 1997; Hill et al. 1998; Liu and Orgel 1998; Lambert 2008; Lambert et al. 2009; Rimola et al. 2009).

Ferris and colleagues (Holm et al. 1993; Ferris et al. 1996; Ertem and Ferris 1996, 1997; Ertem 2002; Ferris 1999, 2005; Ertem et al. 2007, 2008) induced clays to act as scaffolds in the formation of RNA oligomers up to 50-mers. Despite these advances, Orgel (1998) concluded that as more molecules are added to a lengthening polymer the strand becomes more tightly bound to the mineral surface. Such strong adhesion might prove problematic in the production of useful biologically active macromolecules. One possible solution was described by Hanczyc et al. (2003), who mixed clays, RNA nucleotides, and lipids in a single experiment. The clays adsorb RNA while hastening 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.

Smith and coworkers (Smith 1998; Parsons et al. 1998; Smith et al. 1999) have explored an alternative to adsorption on clays by invoking reactions within the channels of mesoporous zeolite minerals. Prebiotic molecules concentrated and aligned inside zeolite channels might undergo polymerization reactions.

The most elaborate mineral-based origins scenario posits that self-replicating clay minerals were, themselves, the first living entities (Cairns-Smith 1968, 1977, 1982, 1985a, 1985b, 1988; Cairns-Smith and Hartman 1986). According to this model, crystal growth defects, 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 could "replicate" by cleaving, whereas 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, according to this hypothesis, organic molecules used clay-life as scaffolding for the evolution of modern biochemistry. Greenwell and Coveney (2006) have proposed a similar model using layered double hydroxides as "information storage and transfer compounds." Recent tests of the crystal gene model by Bullard and coworkers (2007) underscore the experimental difficulties inherent in testing such a model.

CHALLENGES AND FUTURE RESEARCH DIRECTIONS

A central objective of this collection is to move away from classical chemical scenarios that emphasize synthesis of simple organic molecules, and instead treat the origin of life as a pathway extending from the smallest organic molecules to the emergence of molecular systems that can be contained in some form of semi-permeable compartment. An important added emphasis is the consideration of realistic physical and chemical environments of early Earth. Life's origins occurred in a geochemical milieu in which chemically complex constituents at solid-fluid and fluid-fluid interfaces were subjected to chemical and thermal gradients, fluid fluxes, and a variety of cyclic processes.

Recent experiments underscore the potential for these geochemical complexities to enhance significantly organic reaction rates and pathways, as well as the rates and mechanisms of molecular selection, concentration, and self-organization. Thus, these nonequilibrium aspects of dynamic geochemical environments may have been critical to promoting key steps in prebiotic chemical evolution. This article has emphasized possible roles of mineral surfaces in such information transfer.

Opportunities in Mineral Surfaces Research

Studies of mineral-molecule interactions are still in their infancy, but several intriguing observations should inform future work.

1. *Differential adsorption:* It is well known that electrolytes, metals, and organic molecules compete for surface binding sites (e.g., Schindler 1990), but few studies have

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addressed the question of competitive or cooperative biomolecular adsorption. For example, Pontes-Buarques et al. (2001) discovered that while adenosine monophosphate (AMP) alone does not easily adsorb onto pyrite (FeS_2) in the absence of divalent cations, the addition of acetate strongly enhances AMP binding. Such interactive molecular adsorption phenomena could have important implications for life's chemical origins.

Competitive adsorption may also play an important role. Churchill et al. (2004) observed that amino acid adsorption may be highly dependent on mineral surface charge. Quartz ($pH_{PZC} \sim 2.8$) tends to adsorb amino acids most strongly when the mineral pH_{PZC} and the isoelectric point (pI) of the amino acid differ significantly. Thus, quartz adsorbs lysine ($pI = 9.74$) more strongly than amino acids with lower pI (glycine, alanine, aspartate, glutamate, tyrosine, and leucine). In contrast, although calcite ($pH_{PZC} = 9.5$) interacts most strongly with aspartate ($pI = 2.98$) and glutamate ($pI = 3.08$), it also adsorbs a variety of other amino acids with $6 < pI < 10$. Calcite may thus represent a more plausible template than quartz for prebiotic selection and organization of homochiral polypeptides. Similarly, ribose is selectively concentrated on rutile from equimolar solutions of the isomeric pentose sugars: arabinose, lyxose, ribose, and xylose (Hazen 2006; Bielski and Tencer 2006; Cleaves et al. 2009). Additional competitive adsorption experiments, including studies that incorporate realistic sea water salinity, are needed, even though divalent cations in solution may inhibit molecular self-organization in some systems (Monnard et al. 2002).

2. *Molecular Organization*: In the special case of highly planar crystal surfaces, it is sometimes possible to image individual adsorbed molecules or clusters of molecules. In some cases, adsorbed molecules have been found to organize into periodic two-dimensional surface structure—structures that might have played a role in prebiotic chemical evolution. Sowerby et al. (1996, 1998a, 1998b, 2002) used scanning tunneling microscopy to document structures of self-assembled monolayers of adenine and guanine on graphite (C) and molybdenite (MoS_2), Kühnle et al. (2002) imaged individual cysteine dimers adsorbed on gold, and Uchihashi et al. (1999) observed adenine adsorption on graphite with noncontact AFM. AFM studies and molecular calculations also suggest that amino acids can adsorb selectively along linear surface steps of calcite (Orme et al. 2001; de Yoreo and Dove 2004), perhaps providing an alignment conducive to homochiral polymerization (Hazen et al. 2001).

   These results point to the need for in situ studies not just of adsorption, but also of molecular organization and polymerization on mineral surfaces. The potential roles of irregular surface topologies on polymerization (e.g., Elhadj et al. 2006) should also be explored.

3. *Molecular Stabilization*: A significant recurrent objection to any role of hydrothermal systems in life's origins is the rapid decomposition of many important biomolecules at elevated temperatures (Bada et al. 1995; Wills and Bada 2000; Bada and Lazcano 2002; see, however, Shock 1993; Seewald et al. 2006). However, inner-sphere bonding of organic molecules to mineral surfaces may play a significant role in enhancing the thermal stability of these molecules (Hazen 2006; Lambert 2008). For example, it is well known that the inner-sphere (calcium-oxygen) bonding of proteins such as osteocalcin and collagen to hydroxylapatite in bones (e.g., Hoang et al. 2004) can lead to the preservation of these proteins for periods in excess of a million years (Collins et al. 2000; Nielsen-Marsh et al. 2005; Schweitzer et al. 2007). Consequently, much more research needs to be performed on mineral-induced thermal stabilization of biomolecules.

Experimental Design and the Origin of Life

Perhaps the greatest challenge facing origins-of-life researchers is conducting experiments that effectively mimic the complex prebiotic geochemical environment. Origins investigators have long recognized the importance of nonequilibrium characteristics of the prebiotic world and, accordingly, have incorporated some aspects of these geochemical realities into their experiments. The transformational experiments of Miller and Urey (Miller 1953; Miller and Urey 1959) used thermal gradients and fluid fluxes in association with spark discharges to achieve organic synthesis. Subsequent theoretical models (Wächtershäuser 1988, 1990, 1992; de Duve 1995; Russell and Hall 1997, 2006) and experiments (Lahav et al. 1978; Ferris et al. 1996; Huber and Wächtershäuser 1997; McCollum and Simoneit 1999; Whitfield 2009) have incorporated aspects of molecular complexity that may emerge from multi-component geochemical systems with gradients, fluxes, cycles, and interfaces. For example, Budin et al. (2009) have found that lateral thermal gradients in a narrow capillary environment enhance localized concentrations of lipids by orders of magnitude—conditions that foster vesicle formation in the low-temperature zones of the experiment.

Of special note are experiments in molecular evolution, for example of selectively binding RNA aptamers (Ellington and Szostak 1990; Wilson and Szostak 1999) and peptides (Seelig and Szostak 2007). These experiments incorporate chemical complexity, fluxes, interfaces, and cycles of molecular selection, each of which adds information to the system and quickly leads to highly functional molecules (Szostak 2003; Carothers et al. 2004; Hazen et al. 2007). Such selective, cycling environments likely represent an essential aspect of life's origins and evolution.

In the case of experiments on mineral-molecule interactions in an aqueous environment, most experiments to date have focused on a single well-characterized mineral with one solute in water with at most a single electrolyte at room conditions. Such experiments are essential to obtain baseline information on the magnitude and geometry of adsorption for various mineral-molecule pairs. Nevertheless, these studies do not replicate prebiotic complexities, including the multiple electrolytes of seawater, numerous competing organic species in the prebiotic soup, and numerous competing mineral phases and surfaces, all present over a range of temperature, pressure, pH, and solute concentrations.

Added to these challenges are the daunting efforts required to reproduce nonequilibrium geochemical complexities in the laboratory. For example, any attempt to impose a thermal gradient on a chemical experiment adds at least three experimental variables (T_{max}, T_{min}, and distance) that must be specified and controlled throughout an experiment. Imposition of cycles is even more challenging, for it requires control of experimental conditions for the two end-member states of the system, as well as the temporal variables related to cycle lengths and rates of change between these two states. Experiments to simulate geochemical environments in a closed laboratory system may encounter unanticipated problems. For example, initial attempts to mimic the interaction of mineral-rich hydrothermal vents with colder ocean water at the Geophysical Laboratory and elsewhere have been thwarted, because metal sulfides dissolve in regions of hotter fluids and then precipitate and clog the system in cooler portions.

Nevertheless, despite the added experimental complexity of incorporating gradients, fluxes and cycles, these aspects of natural geochemical environments were probably essential to the emergence of biochemical complexity and thus must inform the design of future origins-of-life experiments.

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