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Abstract

Water-rock interactions play a critical role in the origin, existence, and prospects of life. Minerals are sources of energy and nutrients. Life uses aqueous chemical gradients to access and use minerals. Chemical disequilibrium, therefore, represents one type of biotic signature. Life also controls other types of disequilibrium, including isotopic disequilibrium and morphology. Water is a fundamental contributor to all of these biosignatures, acting as a medium for mass transfer and a reservoir for components. Distinguishing biosignatures from abiotic signatures challenges instrumental capabilities. Finally, the ubiquity and heterogenous distribution of life on Earth challenges the ability to interpret different types of disequilibria as evidence for life, or absence thereof.

Keywords: astrobiology, geochemistry, detection of life.

1. Introduction to Signatures of Life

One of the most profound questions is that of whether life existed, exists, or could develop elsewhere in the universe. At present, Earth is our only example of life (N=1). Despite its proximity, gaps remain in the record of life on Earth, particularly for the most ancient examples. Insight from modern life and its environments, communities and processes serves to fill some of those gaps, but research is limited by the ubiquitous occurrence of life on Earth. Natural examples of abiotic environments capable of hosting life are not found on Earth; though organisms may be scarce, they have been found in terrestrial environments characterized by extremes in temperature, pressure, depth, nutrient-availability, and humidity (e.g., [1-3]). Abiotic conditions are only achieved in laboratories and even then may be subject to questions of sterility.

The one thing that is known, however, is that life on Earth requires water, energy, carbon, and other nutrients. These ingredients (except for light as a source of energy) ultimately come from inorganic sources: rock or atmosphere. Water-rock interaction is critical for providing carbon, nutrients, and, at

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least for primitive life forms, energy. Life, then, could be expected to impart some type of chemical or physical signatures as it uses these ingredients, changing them into other forms and consuming the products of water-rock interaction. This paper examines the role of water-rock interaction in the search for signatures of life on Earth and, by extrapolation, to other systems.

1.1. Disequilibrium

Disequilibrium, the departure of system components from their thermodynamically stable phase, is a fundamental characteristic of geological systems as well as biological systems. For the former, disequilibrium derives from physical gradients that, presumably with mixing, can be eliminated over time. Even after 4.6 Ga, the Earth is not homogenous and is not geochemically partitioned according to thermodynamic principles. In many near-surface and surface environments, the latter represents a concerted effort by life to prevent mixing in order to maintain gradients for the purpose of extracting energy and nutrients from the environment. This can be achieved internally by transporting materials across a membrane and externally through the release of reactive substances. Such activities generate disequilibrium in several key, detectable systems, including chemistry, mineralogy, and morphology.

Oxidation-reduction (redox) potential, isotopic distribution and chemical composition are three examples of chemical disequilibrium that life induces in its environment. Redox potential is manipulated by life to extract energy from the environment. This leads to gradients of concentrations of redox pairs, including the energy-rich, unstable redox pair – O_2/H_2O. Evidence for changes in the concentration of O_2 in Earth's atmosphere is found in modern and ancient rocks as differences in the values of S^{2-}/SO_4^{2-} and Fe^{2+}/Fe^{3+} redox pairs as indicated by the presence or absence of minerals, such as pyrite or hematite. Life selects for light isotopes of C along with several other elements. As a consequence, organic carbon tends to have negative $\delta^{12}C/^{13}C$, leaving the remaining inorganic carbon with a heavier isotopic signature.

The presence of organic carbon itself is not necessarily evidence of life because organic compounds are found in many meteorites [4], but isotopic fractionation requires selectivity and energy input, which on Earth is provided by life. Nevertheless, organic compounds are constructed from a restricted group of subunits in living systems, more so than in extraterrestrial materials (e.g., [4-10]). Hence, high concentrations of organic carbon with relatively restricted types of organic structures provide a signature of terrestrial life, at a minimum.

In addition to effects on chemical signatures, disequilibria in morphological and mineralogical signatures provide evidence for terrestrial life. Stromatolites are examples of biogenic structures (Fig. 1); stromatolites are laminated rocks in which the laminae differ mineralogically and chemically as a direct consequence of microbial activities. Ancient stromatolites document the expansion of life to many environments (e.g., [11]) while modern stromatolites are restricted to extreme environments (e.g., [12]). Such morphological structures can be signatures of life if their formation is strictly biologically mediated (e.g., [11, 13]); biota use energy to control otherwise entropic depositional processes. Life also provides templates for mineral formation that are unique; biogenic minerals and mineraloids have characteristics that cannot be replicated in abiotic systems [14]. For example, echinoderms and diatoms use organic templates to dictate deposition of optically monocrystalline calcite and amorphous opal, respectively; disorder would dominate in a thermodynamically driven system with some exceptions [15].
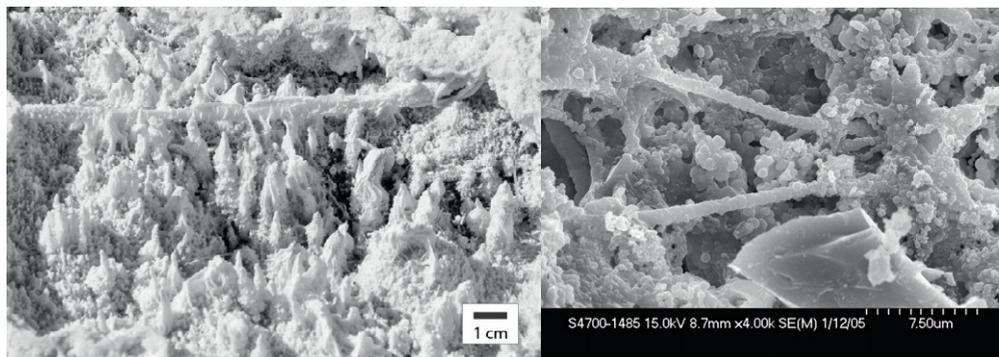
Fig. 1. Left: Modern stromatolites, Mammoth Hot Springs, Yellowstone National Park, WY, USA. *Photo credit M. Gonsior.* Right: SEM photomicrograph of geyserite, Trinoi Geyser, Kamchatka, Russia.

2. Role of Water-Rock Interaction

Water is the medium of formation for all of these biosignatures, although it may not be necessary for an abiotic equivalent. Indeed, weathering reactions themselves require water, usually at least slightly acidic. It is these weathering reactions that release nutrients (e.g., P and trace elements) necessary for life. The amount and chemistry of aqueous solutions often determine the type, amount, and properties of the resulting biosignature.

Reaction rates are controlled partly by solution chemistry; solution chemistry partly controls the formation of excited states and stability of intermediate states. Biological processes circumvent these controls by routing reactions through lower excitation thresh-holds and different intermediates. Enzymes control the sequence of steps, leading to more limited reaction products and minimizing the effects of solution chemistry on mineralogy. For example, iron oxides, oxyhydroxides, and sulfates form during weathering of igneous rocks, among other types. Iron oxidation under acidic conditions is extremely slow [16]; pH-dependent hydrolysis products react more quickly than the aqueous ion (1), and reduced iron can persist for long periods in low humidity regardless of pH. Biological processes mediate oxidation under acidic conditions, so ferric iron oxides in low-temperature acidic environments could be an indicator of the presence of life and water, although such evidence would be insufficient to demonstrate the presence of either life or water.

$$-dFe^{2+}/dt = 6 \times 10^{-5}[Fe^{2+}] + 1.7[Fe(OH)^+] + 4.3 \times 10^{5}[Fe(OH)_2^0] \qquad (1)$$
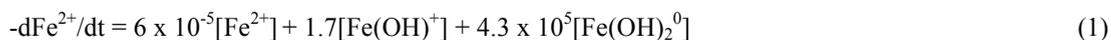
Because many low-temperature reactions have solution-precipitation mechanisms, water provides a medium for isotopic exchange of carbon, sulfur, oxygen, hydrogen, and nitrogen as a reaction progresses. The amount of water relative to the amount of rock contributes to the fractionation of isotopes in geological systems. This water-rock ratio determines the isotopic reservoir from which life removes, selectively or not, elements for energy, structure, and metabolic purposes. Biological processes selectively use the lighter isotopes, further enhancing isotopic fractionation in geological systems.

Chemical signatures generally take the form of large organic compounds, although many types of organic compounds, some of which are large and complex, are found in meteorites and are formed abiotically [5, 6, 9, 17]. Natural organic matter matures first to kerogen and eventually to graphite under appropriate conditions. The maturation process is thought to proceed by both condensation reactions and by loss of functional groups. Immiscibility between water and non-polar organic compounds serves to concentrate the latter as the former forces it to migrate according to density, leaving more recalcitrant organic matter in place. Although neither the presence of nor the concentration of organic matter is definitive for the presence of life, organic compounds are the 'gold-standard' for life detection.

Morphological signatures, e.g., stromatolites, most often form from mineral precipitation from aqueous solutions. The solutions are either inherently saturated or reach saturation through biological processes. Examples of the former include silica-saturated hot spring solutions that precipitate sinter or geyserite, entombing microbes in the process, or iron oxide accumulation in drainages made oversaturated and acidic by microbial oxidation of pyrite. Examples of the latter generally involve precipitation of carbonate minerals, made oversaturated by removal of CO_2 during synthesis of organic matter. In either case, morphological signatures preserve microbial cells, filaments, and extracellular polymeric substances during mineralization process. However, morphological signatures are not definitive as evidence for life unless the process by which they form has a causal relationship with biological processes [13, 15].

Mineralogical signatures occur when the properties of an authigenic hydrogenous mineral show evidence of biological influence. Examples include cell dimensions or habit [18], in magnetite [19], jarosite [20], and calcite (e.g., [21, 22]. In these examples, minerals formed in the presence of life exhibit different properties than minerals formed in abiotic controls. In some cases, these defects change the reactivity of the mineral [23] by inducing chemical or structural defects. Minerals, with or without structural defects, are also catalysts for reactions that modify organic matter or change the chemical environment (e.g., [24, 25]). So higher concentrations of certain reaction products may provide some indirect evidence of biological influence. Minerals also can store biological information in the form of biomolecules incorporated into or onto the minerals [26-28], making these minerals excellent targets for exploration for life. Precipitation from water provides a mechanism by which life can influence the properties of minerals.

3. Challenges

The ubiquitous nature of life on Earth is a primary challenge to determination of definitive evidence for life. Laboratory experiments provide reasonable controls on the influences of life on isotopic, chemical, mineralogical, and morphological signatures, but these experiments cannot be easily verified in natural environments.

The primary limitation is instrumental detection limits. Spatial limitations are imposed by electronic limitations; the electronic detection limit determines the amount of analyte that can be detected and therefore the sample size required. If concentrations are spatially heterogenous then the analyte signal can be lost in the noise [29]. As instrumental resolution and detection limits improve, the ability to distinguish biosignatures from abiotic products will increase understanding of life's origin and evolution.

4. Conclusions

Water and life are inextricably linked on Earth because water is an important solvent, allowing access to required nutrients made available through chemical weathering. This relationship applies to life on Earth and may or may not apply to life elsewhere in the universe. In the absense of photosynthesis, life must take advantage of other energy sources, one of which is chemical energy made available along

gradients as a consequence of kinetic controls and changing physical conditions. Water provides a medium for other types of thermodynamic signatures, including isotopic and morphological signatures. Fractionation of isotopes is not solely controlled by biological activity; photochemical, kinetic, and mass-dependent fractionation occurs abiotically. However, for biologically active elements, life controls isotopic fractionation by favoring lighter isotopes. Distinguishing biosignatures from abiotic signatures can be instrumentally challenging because of the balance between spatial resolution and detection limits; higher spatial resolution requires greater detection limits. Finally, the ubiquity and heterogenous distribution of life on Earth challenges the ability to interpret different types of disequilibria as evidence for life or absence thereof.

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