

Water on Mars and the Prospect of Martian Life

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vidence of water on Mars dates back to the first observations of channeled landscapes made by Mariner 9 and Viking. More recent images from Mars Global Surveyor and Mars Express strikingly confirm that fluids have sculpted the Martian surface at least episodically through its history. The Mars Exploration Rovers Opportunity and Spirit have added evidence for extensive rock-water chemical interactions in the regions where these remote geologists landed, while OMEGA and THEMIS have shown that similar processes took place in many parts of the planet.

Because of the close relationship between water and biological activity on Earth, such observations have been taken as hopeful signs that Mars, as well, might once have supported life and, indeed, might still do so in subterranean oases. There is, however, much more to consider. Water appears to be necessary for life, at least as it exists on Earth and can be contemplated on Mars, but it does not, by itself, insure habitability. In this paper, we review the broader requirements for biological activity as they relate to water and use these to constrain astrobiological inferences about Mars.

KEYWORDS: Mars, Meridiani, water, life, astrobiology

WHY IS WATER KEY TO RECIPES FOR LIFE?

In chemistry, geometry is destiny, and it is the distinctive molecular geometry of H_2O that accounts for many of its biofriendly attributes (Finney 2004). In water molecules, a relatively large oxygen nucleus is flanked by two smaller, asymmetrically placed hydrogen nuclei, forming a distinctly

polar molecule with a mean HOH angle of 104.5°. Because of their pronounced dipole moment, water molecules interact strongly with one another via hydrogen bonding. Not only do these molecular interactions determine the crystallographic structure of ice, which famously (and, from a biological standpoint, usefully) floats in water, they also explain why H_2O is liquid at temperatures where most comparably small molecules are gases.

Water ionizes readily, resulting in anomalously high rates of molecular diffusion and a pronounced capacity to conduct excess protons (Finney 2004). Also, water effectively dissociates ionic species. Thus, water provides a particularly

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² Division of Geological and Planetary Sciences California Institute of Technology Pasadena CA 91125, USA E-mail: grotz@gps.caltech.edu Water, water, every where, And all the boards did shrink; Water, water, every where, Nor any drop to drink.

"Rime of the Ancient Mariner" Samuel Taylor Coleridge

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favorable medium for the chemistry of life. At temperatures typical of the Earth's surface, liquid water coexists with gaseous CO₂, N₂, O₂, H₂S, and NH₃; it can accumulate relatively high concentrations of CO32-, HCO3-, HS-, SO42-, NH4+, Fe²⁺, and other ions in solution; it carries dissolved organic molecules stably in solution; and it interacts strongly at polar interfaces. Thus, water provides a medium in which carbon and the other chemical ingredients of life can interact with one another and, in a biological world, with organisms.

Water may not be unique in this respect—it has been suggested that ammonia, formamide, and several other organic compounds might function as biopermissive fluids at the right temperature and pressure

(Benner et al. 2004). But such compounds are, at best, trivially important as fluid environments on Earth and are doubtfully more relevant to Mars. The fact that water molecules interact in complex and specific ways with enzymes (e.g. Rand 2004) might be taken as further evidence for the unique fit between H_2O and life, but this

> may tell us only that life on Earth has evolved to maximize biochemical function in an aqueous milieu (Ball 2005).

WHY THERE IS MORE TO THE RECIPE

Nutrients

Water may be necessary for biological activity, but as the plight of the Ancient Mariner illustrates, it is certainly not sufficient. Terrestrial life is based on carbon, and collec-

sumferni. Forestrial life is based on earbon, and concetively, C, H, and O make up nearly 80% of the dry weight of a bacterial cell. ("Dripping wet," bacteria are about 70% water.) Cells, however, contain many additional elements more than thirty in typical microorganisms. Other major constituents include N and P, with cellular C:N:P lying near 106:16:1 (what biologists call the Redfield ratio). N and P find obligate use in proteins, membranes, and nucleic acids, the fundamental structural, functional, and informational molecules of the cell. It is by no means clear that the same molecules will characterize life wherever we may find it, but it is hard to conceive of functional and informational macromolecules that do not contain N or P. Sulfur also plays key roles in cells, notably in S–S bonds that govern the three-dimensional conformation of proteins and FeS clusters that form the functional heart of some ancient and critically important enzymes. Indeed, De Duve (1995) has speculated that thioesters played a crucial role in the origin of life on Earth. For these reasons, life likely can form and persist only on planets where N, P, and possibly S are present in biologically available forms.

Other elements are required in minor or trace abundances. For example, Fe and, in many organisms, Mo are essential cofactors in biological fixation of nitrogen. Mo is required, as well, by organisms that use nitrate as a source of N for proteins, nucleic acids, and other biomolecules. Thus, on Earth there could be no biological nitrogen cycle without metal ions available in solution. Mg occupies the structural and functional center of chlorophyll, while Mn atoms mediate the extraction of electrons from water by plants and algae. Similarly, then, without Mg and Mn, photosynthesis as we know it could not exist. Fe plays a central role in hemoglobin, extending the metabolic role of metals to respiration. The recipe for life, then, is complex, and likely has been from the beginning-metallic cofactors have been implicated in many prebiotic chemical reactions and in purportedly primitive biochemical reactions (Williams and Fraústo da Silva 1996). The origin and long-term persistence of life requires not only water, but adequate supplies of major, minor, and trace elements, whose availability will be determined by source rocks and their chemical weathering, as well as by pH, redox, and other environmental parameters. Thus, while water sparked early astrobiological interest in Mars, we have come to the point in planetary exploration where a far more sophisticated understanding of environmental geochemistry is required.

Water Activity

Clearly, environments where life can thrive do not contain pure H₂O, but an aqueous solution of ionic and dissolved organic constituents. Through their interactions with water molecules, however, these substances limit the availability of H₂O for hydration reactions, and at high concentrations, ions and organic molecules can inhibit cellular physiology. Water activity is the effective water content of a solution (in the notation used by microbiologists, $a_w = n_1/(n_1 + n_2)$, where n_1 equals moles of water and n_2 equals moles of solute; Grant 2004). Most terrestrial organisms cannot grow and reproduce at water activities below 0.9. A few bacteria grow where a_w is as low as 0.85, and some archaea can live at an $a_{\rm w}$ of 0.75 (the water activity of a halite-saturated solution). In terms of this parameter, however, fungi define the limits of life: one remarkable species has been shown to grow at $a_w = 0.61$ (Grant 2004). (Honey has such a long shelf life because its water activity falls below the limit for microbial spoilage.) The important point is that in brines where a_w is persistently low, water may be present but uninhabitable.

The Persistence of Water

Regardless of their ability to persevere at chronically low water activities, many organisms—from bacteria to animals—can tolerate episodic dryness. Desiccation-tolerant organisms persist in a dormant state, forming spores, glyco-protein capsules, or other structural phases that retard water loss.

The key variable is the return time of habitable water. Endolithic lichens in Antarctic boulders are metabolically active only a few weeks each year, but it is enough for populations to persist over geological time scales (Friedmann et al. 1993). Cyanobacteria, dried onto herbarium sheets in the nineteenth century, resume photosynthesis almost immediately upon wetting. Even lotus seeds preserved in lake beds from China have been germinated successfully after 1288 ± 271 years (radiocarbon dates) of dormancy (Shen-Miller et al 1995).

Scientists have reported much longer dormancy in bacteria from Pleistocene permafrost and longer still in salt deposits formed more than 250 million years ago. Such claims are controversial—even dormant cells must expend energy now and again to repair molecular damage such as spontaneous DNA breakage. But these reports underscore the fact that we cannot yet place a precise limit on the duration of cellular dormancy. Nor do we know with confidence what biochemical features account for prolonged dormancy in organisms that exhibit this trait.

Regardless of this uncertainty, the time scale of return for liquid water must loom as a key variable in ongoing assessments of Martian habitability. Playas that receive water once every decade likely persist as habitable environments indefinitely; those that recharge once every ten million years may not—unless there exists a reservoir of populations elsewhere that can recolonize ambient waters whenever they reappear.

This latter point is worth underscoring. On Earth, habitable extremes exist in the context of "normal" environments that provide nutrient subsidies and persistent reservoirs of colonizing populations. Maintenance of a viable biota may be far more difficult on planets where environments at or near the extremes of habitability are the *most* favorable sites for life.

Acidity

On Earth, the habitability of aqueous environments is influenced by additional factors, including pH, Eh, and temperature (Knoll and Bauld 1989). Acidity is particularly relevant because geochemical data from Meridiani Planum indicate that sulfuric acid was present when Meridiani sedimentary rocks formed (McLennan et al. 2005). Places like Rio Tinto, Spain, where strongly acidic waters deposit jarosite and iron oxides, provide insights into acid tolerance (FIG. 1, Fernández-Remolar et al. 2005). Acid-tolerant populations thrive in such environments, not because they can run their biochemistry at low pH, but because they efficiently expel protons from their cytoplasm, enabling cell chemistry to continue under more or less neutral conditions.

Acid and desiccation tolerance are not universal attributes of terrestrial organisms, and most groups that accommodate these environmental challenges are descended from ancestors that tolerated them poorly. On Earth, then, life can persist in arid, oxidizing, and acidic habitats, but it might not do so if those were the *only* habitable environments on the planet. Moreover, accumulated data on prebiotic chemistry suggest that life could not have *arisen* under such conditions (Knoll et al. 2005).

ASTROBIOLOGY AND THE RECORD OF WATER ON MARS

Geomorphological and Sedimentological Observations

Much of the ancient cratered terrain of Mars is dissected by small valley systems similar to terrestrial river networks (Baker and Milton 1974). Because significant precipitation and surface runoff are not possible under modern conditions, some researchers have interpreted the valley networks as evidence of warmer, more humid ancient climates (Carr 1996). Alternatively, these drainage patterns could have been created through venting of underground water to the surface, events hypothesized to have been vigorous, but short-lived (Baker and Milton 1974). More recently, the discovery of a channelized alluvial fan northeast of Holden crater has provided evidence for deposition of loose sediment under aggrading conditions (Malin and Edgett 2003) within well-developed meandering channels—water flowed freely across the fan surface. The characteristic time scale for such deposits leads to a minimum estimate for the volume (900–5000 km³) and duration (50–1000 yrs) of water flow (Jerolmack et al. 2004). This modest estimate does not require precipitation, so long as a local source of water is present.

Geomorphological evidence for larger and longer-lived water bodies remains controversial (Baker and Milton 1974). Most recently, high-resolution images of the Elysium region obtained by Mars Express have indicated the possible presence of pack ice preserved beneath a mantle of soil (Murray et al. 2005). In this interpretation, a lake or shallow sea perhaps 50 m deep formed during catastrophic eruption of groundwater from nearby fractures, only to freeze partially, generating pack ice that subsequently became embedded in a larger ice body. Alternatively, these features may be rafts of frozen lava which floated atop a larger pool of igneous melt that flash-froze to preserve the observed geometry. Even if the water–ice hypothesis proves correct, however, liquid water need not have been stable for long intervals (>1000s of years) on the Martian surface.

Ground-based observations by the Mars Exploration Rovers provide considerable insight into the mechanisms by which sulfate minerals may have formed on Mars. Opportunity images provide compelling evidence for the accumulation of sediment particles—formed of admixtures of sulfate salts and silicate minerals—in a variety of sedimentary depositional environments. Eolian strata are capped by interdune fluvial strata that document shallow overland flows with moderate flow velocities (Fig. 2, Grotzinger et al. 2005). Further evidence for an active water table is found in stratigraphically restricted zones of recrystallization and secondary porosity, millimeter-scale hematitic concretions, and millimeter-scale crystal molds that cut across primary layering (McLennan et al. 2005).

Geochemical Observations

The Mars Exploration Rover Opportunity has discovered jarosite $[(K, Na, H_3O)(Fe_{3-x}Al_x)(SO_4)_2(OH)_6, \text{ where } x < 1]$ in Meridiani outcrop rocks, while its mechanical twin Spirit found goethite [FeO(OH)] in Gusev crater; both minerals form in the presence of water (Klingelhöfer et al. 2004, 2005). Elemental abundances indicate that Ca and Mg sulfates occur with the jarosite at Meridiani, although their precise mineralogy cannot be ascertained (Clark et al. 2005). Mars Express has identified gypsum (CaSO₄•2H₂O), kieserite (MgSO₄•H₂O), and, possibly, other polyhydrated sulfates on the Meridiani plain and more widely on the Martian surface (Gendrin et al. 2005). Finally, as noted above, Opportunity has confirmed the presence of hematite at Meridiani, most conspicuously as millimeter-scale concretions that formed during early diagenesis of sulfate-rich sediments (McLennan et al. 2005). Thus, geochemical measurements at outcrop level confirm and extend geomorphological and sedimentological evidence for water on the ancient surface of Mars.

Climate Evolution

The climatic history of Mars since the end of heavy bombardment (ca. 3.8 Ga) is clearly controversial. Some hold that oceans persisted episodically long after bombardment ended. Others argue that while Noachian oceans existed, the Martian surface froze near the end of heavy bombardment and has remained that way ever since. Indeed, based on the thermochronology of Martian meteorites, Shuster and Weiss (2005) claim that Mars has not seen temperatures significantly above freezing for the past four billion years.

We can reconcile geochemical and geomorphological evidence for liquid water with subzero Martian tempera-

FIGURE 1 Blood red waters of Rio Tinto, southwestern Spain. Ferric iron colors this highly acidic river (pH 0.9 to 3); the orange precipitates are comprised of jarosite, schwertmannite, and other iron sulfate minerals, as well as nanophase iron oxides (Fernández-Remolar et al. 2005).





tures in a simple way: by invoking antifreeze. Salts, present in abundance at Meridiani Planum, would lower the freezing temperatures of ambient waters, as would sulfuric acid. Dilute aqueous solutions of sulfuric acid can depress the freezing temperature of water by as much as 70°C, providing a particularly effective way of reconciling diverse observations of Martian environments through time (Knoll et al. 2005).

Considered collectively, and conservatively, there are no geomorphological, geochemical, or sedimentological features yet discovered on Mars that cannot be accounted for by intermittent, short-term flow of surface water, supplied by underground sources and dispersed in a cold, dry climatic regime. The simple observation that channels cut early in Mars history persist to the present tells us that surface water flow has been limited for a long time. This does not eliminate the possibility of a persistently warm, wet Mars in Noachian time, but does emphasize that evidence to support such a model remains meager (Gaidos and Marion 2003).

DISCUSSION

Mars today is a forbidding place. Temperature and atmospheric pressure lie near the triple point of water—indeed liquid water is not stable on the present-day Martian surface (Gaidos and Marion 2003). The surface is also chemically harsh and subject to strong radiation. It is doubtful that organisms thrive today at the Martian surface.

From the preceding paragraphs, one might well conclude that surface environments have been biologically challenging for most of Mars' history. The salty dunes and transient interdune streams that covered Meridiani Planum three to four billion years ago indicate that while chemical weathering and erosion provided many of the elements required for life, ambient environments were arid, acidic, and oxidizing (Knoll et al. 2005). Terrestrial ecology suggests that microorganisms could survive many aspects of the inferred Meridiani environment, but habitability would depend critically on the time scale of water with sufficiently high water activity to support cell biology-a parameter that is currently unknown. Meridiani waters may have been habitable upon introduction, but water activity would have dipped below habitable levels as groundwater, playas, or both, evaporated to dryness.

Whether Meridiani is broadly representative of the Martian surface three to four billion years ago is unknown, but remote sensing from Mars Express suggests that it could FIGURE 2 A seven-meter section of sedimentary rocks exposed within Endurance crater, Meridiani Planum, Mars. These rocks, the first sedimentary succession ever examined at outcrop scale on Mars, preserve a record of ancient water. Large-scale cross-bedding visible in the lower left indicates the passage of ancient sand dunes. These cross-bedded deposits are overlain by laminated sand sheet deposits also formed by wind-blown sand; however, the overlying sed-iments include cross-laminated, rippled beds deposited by shallow, sub-aqueous flows. The dark band visible near the top of the succession is interpreted to have formed during alteration and cementation of the sediments by percolating groundwater.

be—equally, it could be unusually *favorable* from an astrobiological perspective. All in all, the aqueous deposits of Meridiani Planum are biologically permissive, but they may record the sunset of a habitable Martian surface, not its beginning.

The briny acidic waters of Meridiani Planum would certainly constitute a formidable challenge to the types of prebiotic chemical reactions thought to have played a role in the origin of life on Earth (Knoll et al. 2005). This is a relevant consideration because heavy bombardment could have eradicated any surficial life that evolved during Mars' earliest history. One might argue that Mars could have been (re?)colonized after late heavy bombardment by organisms transported by meteorites from Earth. The physical mechanism is plausible—the key question, however, is: what is the probability that terrestrial colonists would have landed in a Martian environment that could support sustained metabolism?

The most promising places to look for evidence of surface life on Mars are probably sedimentary basins that preserve a record of Mars' earliest history, when water was most abundant and persistent and both oxidation and acidity were least developed. We know relatively little about such terrains, but they would seem prime candidates for future missions aimed at understanding Mars' environmental history, as well as astrobiology.

The Subsurface Alternative

If surface environments on Mars have been challenging for life for the past several billion years, what about the subsurface? There is inherent skepticism when environments deemed most likely to support life are those least amenable to observation. Nonetheless, the subsurface was (and may still be) the most likely place on Mars to find persistent reservoirs of liquid water. Given a continuing supply of nutrients (which introduces its own set of challenges), life in the Martian crust might be sustained by a primordial hydrogen economy—chemical energy in the form of H_2 produced by aqueous alteration of basalts.

The only Martian rocks known to contain carbonate minerals are meteorites that preserve iron and magnesium carbonates precipitated in subsurface cracks flushed by groundwater (McKay et al. 1996; Bridges and Grady 2000). Sulfide minerals formed as well, indicating that at least some subsurface environments were neither acidic nor oxidizing early in Martian history. At present, however, we know little about water activity or persistence in such environments.

Several laboratories have reported methane emissions from the Martian surface (Krasnopolsky et al. 2004; Formisano et al. 2005), and the argument has been advanced that these exceed fluxes expected for abiotic methanogenesis (Krasnopolsky et al 2004). Hydrothermal alteration of crustal rocks may, however, be sufficient to explain the reported fluxes (Lyons et al. 2005). Moreover, the proximal source of methane (if correctly identified) need not be limited to current biological or hydrothermal processes. Possibly, current methane fluxes reflect release from permafrost as it sublimes, decoupling current emanations from physical processes of formation.

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The Future

In future exploration, astrobiologists need to learn about the time scales on which water has persisted on Mars, and geochemical analyses must be extended to include nutrients, especially nitrogen in Martian soils. Better models and experiments can sharpen our sense of water activity during the deposition and early diagenesis of Meridiani-type sedimentary rocks, while future orbital and lander missions will tell us the extent to which such environments were representative of the early Martian surface. Was ancient Mars *generally* arid, acidic, and oxidizing, and if so, when did it become that way?

Of course, the biggest hurdle for astrobiology concerns biology, itself. To what extent can we generalize from observations of the only biological planet we know? That problem will not be solved soon, meaning that the search for evidence of life elsewhere will remain empirical and difficult. But as future missions provide improved data on the environmental history of Mars, we may yet learn whether life on Earth is unique or merely uniquely successful in our solar system.

ACKNOWLEDGMENTS

We thank NASA's Mars Exploration Rover project for support and MER's engineers and scientists for the extraordinary mission that made this paper possible.

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