INTRODUCTION

Habitability, Taphonomy, and the Search for Organic Carbon on Mars

THE QUEST FOR EXTRATERRESTRIAL LIFE IS AN OLD AND INEVITABLE ambition of modern science. In its practical implementation, the core challenge is to reduce this grand vision into bite-sized pieces of research. In the search for organic remnants of past life, it is enormously helpful to have a paradigm to guide exploration. This begins with assessing habitability: Was the former environment supportive of life? If so, was it also conducive to preservation of organism remains, specifically large organic molecules?

The 2004 arrival of the Mars Exploration Rovers (MERs) Spirit and Opportunity provided a chance to investigate ancient aqueous envi-

ronments in situ and deduce their likelihood of supporting life. Initial results confirmed what data from orbiters had long suggestedthat diverse aqueous environments existed on the surface of Mars billions of years ago. The success of the MERs led to the development of the Mars Science Laboratory (MSL) mission. The Curiosity rover landed at Gale crater in 2012 and was designed to specifically test whether ancient aqueous environments had also been habitable. In addition to water, did these ancient environments also record evidence for the chemical building blocks of life (C, H, N, O, P, S), as well as chemical and/or mineralogic evidence for redox gradients that would have enabled microbial metabolism, such as chemoautotrophy? Curiosity also has the capability to detect organic carbon, but it is not equipped for life detection.

Five articles presented in full in the online edition of *Science* (www.sciencemag.org/ extra/curiosity), with abstracts in print (pp. 387–389), describe the detection at Gale crater of a system of ancient environments (including streams, lakes, and groundwater networks) that would have been habitable by chemoautotrophic microorganisms. The Hesperian age (<~3.7 billion years) rocks mentioned in these articles are at the young end of the spectrum of ancient martian aqueous

Image taken by the Mars Hand Lens Imager of the John Klein drill hole (1.6 cm in diameter) at Yellowknife Bay reveals gray cuttings of mudstone (ancient lake sediments), rock powder, and interior wall. An array of eight ChemCam laser shot points can be seen. The gray color suggests that reduced, rather than oxidized, chemical compounds and minerals dominated the pore fluid chemistry of the ancient sediment. A cross-cutting network of sulfate-filled fractures indicates later flow of groundwater through fractures after the sediment was lithified.

environments. Yet, a sixth article details a more ancient and also potentially habitable environment detected in Noachian age (>~3.7 billion years) rocks at Meridiani Planum. A seventh article describes the present radiation environment on the surface of Mars at Gale crater and its influence on the preservation of organic compounds in rocks.

Opportunity landed at Meridiani Planum on 25 January 2004. Coincident with the 10th anniversary of this landing, Arvidson *et al.* report the detection of an ancient clay-forming, subsurface aqueous environment at Endeavour crater, Meridiani Planum. Though Opportunity does not have the ability to directly detect C or N, it has been able to establish that several of the other key factors that allow for the identification of a formerly habitable environment were in place. This potentially habitable environment stratigraphically underlies and is considerably older than the rocks detected earlier in the mission that represent acidic, hypersaline environments that would have challenged even the hardiest extremophiles. The presence of both Fe⁺³- and Al-rich smectite clay minerals in rocks on the rim of the Noachian age Endeav-

our impact crater were inferred from the joint use of hyperspectral observations by the Mars Reconnaissance Orbiter and extensive surface observations by the Opportunity rover. The rover was guided tactically by orbiter-based mapping. Extensive leaching and formation of Al-rich smectites occurred in subsurface groundwater fracture systems.

Grotzinger et al. show that an ancient habitable environment existed at Yellowknife Bay, Gale crater, where stream waters flowed from the crater rim and pooled in a curvilinear depression at the base of Gale's central mountain to form a lake-streamgroundwater system that might have existed for millions of years. Vaniman et al. provide evidence for moderate to neutral pH, as shown by the presence of smectite clay minerals and the absence of acid-environment sulfate minerals, and show that the environment had variable redox states due to the presence of mixed-valence Fe (magnetite) and S (sulfide, sulfate) minerals formed within the sediment and cementing rock. McLennan et al. show that lake salinities were low because of the very low concentration of salt in the lake deposits. Elemental data indicate that clays were formed in the lake environment and that minimal weathering of the crater rim occurred, suggesting

that a colder and/or drier climate was prevalent.

Ming *et al.* show that the thermal decomposition of rock powder yielded NO and CO_2 , indicating the presence of nitrogen- and carbonbearing materials. CO_2 may have been generated by either carbonate or organic materials. Concurrent evolution of O_2 and chlorinated hydrocarbons indicates the presence of oxychlorine species. Higher abundances of chlorinated hydrocarbons in the lake mudstones, as compared with modern windblown materials, suggest that indigenous martian or meteoritic organic C sources are preserved in the mudstone. However, the possibility of terrestrial background sources brought by the rover itself cannot be excluded.

These results demonstrate that early Mars was habitable, but this does not mean that Mars was inhabited. Even for Earth, it was a formidable challenge to prove that microbial life existed billions of years ago—a discovery that occurred almost 100 years after Darwin predicted it, through the recognition of microfossils preserved in silica (1). The trick was finding a material that could preserve cellular structures. A future mission could do the same for Mars if life had existed there. Curiosity can help now by aiding our understanding of how organic compounds are preserved in rocks, which, in turn, could provide guidance to narrow down where and how to find materials that could preserve fossils as well. However, it is not obvious that much organic matter, of either abiologic or biologic origin, might survive degradational rock-forming and environmental processes. Our expectations are conditioned by our understanding of Earth's earliest record of life, which is very sparse.

Paleontology embraces this challenge of record failure with the subdiscipline of taphonomy, through which we seek to understand the preservation process of materials of potential biologic interest. On Mars, a first step would involve detection of complex organic molecules of either abiotic or biotic origin; the point is that organic molecules are reduced and the planet is generally regarded as oxidizing, and so their preservation requires special conditions. For success, several processes must be optimized. Primary enrichment of organics must first occur, and their destruction should be minimized during the conversion of sediment to rock and by limiting exposure of sampled rocks to ionizing radiation. Of these conditions, the third is the least Earth-like (Earth's thick atmosphere and magnetic field greatly reduce incoming radiation). Curiosity can directly measure both the modern dose of ionizing cosmic radiation and the accumulated dose for the interval of time that ancient rocks have been exposed at the surface of Mars.

Hassler *et al.* quantify the present-day radiation environment on Mars that affects how any organic molecules that might be present in ancient rocks may degrade in the shallow surface (that is, the top few meters). This shallow zone is penetrated by radiation, creating a cascade of atomic and subatomic particles that ionize molecules and atoms in their path. Their measurements over the first year of Curiosity's operations provide an instantaneous sample of radiation dose rates affecting rocks, as well as future astronauts. Extrapolating these rates over geologically important periods of time and merging with modeled radiolysis data yields a predicted 1000-fold decrease in 100–atomic mass unit organic molecules in ~650 million years.

Sediments that were buried and lithified beneath the radiation penetration depth, possibly with organic molecules, would eventually be exhumed by erosion and exposed at the surface. During exhumation, organics would become subject to radiation damage as they entered the upper few meters below the rock-atmosphere interface. The time scale of erosion and exhumation, and thus the duration that any parcel of rock is subjected to ionizing radiation, can be determined by measuring cosmogenically produced noble gas isotopes that accumulate in the rock. ³⁶Ar is produced by the capture of cosmogenic neutrons by Cl, whereas ³He and ²¹Ne are produced by spallation reactions on the major rock-forming elements. Farley *et al.* show that the sampled rocks were exposed on the order of \sim 80 million years ago, suggesting that preservation of any organics that accumulated in the primary environment was possible, although the signal might have been substantially reduced.

Wind-induced saltation abrasion of the rocks in Yellowknife Bay appears to have been the mechanism responsible for erosion and exhumation of the ancient lake bed sampled by Curiosity. The geomorphic expression of this process is a series of rocky scarps that retreated in the downwind direction. Understanding this process leads to the prediction that rocks closest to the scarps were most recently exhumed and are thus most likely to preserve organics, all other factors being equal. In this manner, the MSL mission has evolved from initially seeking to understand the habitability of ancient Mars to developing predictive models for the taphonomy of martian organic matter. This parallels the previous decade, in which the MER mission turned the corner from a mission dedicated to detecting ancient aqueous environments to one devoted to understanding how to search for that subset of aqueous environments that may also have been habitable.

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ABSTRACTS

Ancient Aqueous Environments at Endeavour Crater, Mars

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Opportunity has investigated in detail rocks on the rim of the Noachian age Endeavour crater, where orbital spectral reflectance signatures indicate the presence of Fe⁺³-rich smectites. The signatures are associated with finegrained, layered rocks containing spherules of diagenetic or impact origin. The layered rocks are overlain by breccias, and both units are cut by calcium sulfate veins precipitated from fluids that circulated after the Endeavour impact. Compositional data for fractures in the layered rocks suggest formation of Al-rich smectites by aqueous leaching. Evidence is thus preserved for water-rock interactions before and after the impact, with aqueous environments of slightly acidic to circum-neutral pH that would have been more favorable for prebiotic chemistry and microorganisms than those recorded by younger sulfate-rich rocks at Meridiani Planum.

>> Read the full article at http://dx.doi.org/10.1126/science.1248097

Reference

S. A. Tyler, E. S. Barghoorn, Occurrence of structurally preserved plants in Pre-Cambrian rocks of the Canadian Shield. *Science* 119, 606–608 (1954).

A Habitable Fluvio-Lacustrine Environment at Yellowknife Bay, Gale Crater, Mars

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The Curiosity rover discovered fine-grained sedimentary rocks, which are inferred to represent an ancient lake and preserve evidence of an environment that would have been suited to support a martian biosphere founded on chemolithoautotrophy. This aqueous environment was characterized by neutral pH, low salinity, and variable redox states of both iron and sulfur species. Carbon, hydrogen, oxygen, sulfur, nitrogen, and phosphorus were measured directly as key biogenic elements; by inference, phosphorus is assumed to have been available. The environment probably had a minimum duration of hundreds to tens of thousands of years. These results highlight the biological viability of fluvial-lacustrine environments in the post-Noachian history of Mars.

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Mineralogy of a Mudstone at Yellowknife Bay, Gale Crater, Mars

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Sedimentary rocks at Yellowknife Bay (Gale crater) on Mars include mudstone sampled by the Curiosity rover. The samples, John Klein and Cumberland, contain detrital basaltic minerals, calcium sulfates, iron oxide or hydroxides, iron sulfides, amorphous material, and trioctahedral smectites. The John Klein smectite has basal spacing of ~10 angstroms, indicating little interlayer hydration. The Cumberland smectite has basal spacing at both ~13.2 and ~10 angstroms. The larger spacing suggests a partially chloritized interlayer or interlayer magnesium or calcium facilitating H₂O retention. Basaltic minerals in the mudstone are similar to those in nearby eolian deposits. However, the mudstone has far less Fe-forsterite, possibly lost with formation of smectite plus magnetite. Late Noachian/Early Hesperian or younger age indicates that clay mineral formation on Mars extended beyond Noachian time.

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Elemental Geochemistry of Sedimentary Rocks at Yellowknife Bay, Gale Crater, Mars

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Sedimentary rocks examined by the Curiosity rover at Yellowknife Bay, Mars, were derived from sources that evolved from an approximately average martian crustal composition to one influenced by alkaline basalts. No evidence of chemical weathering is preserved, indicating arid, possibly cold, paleoclimates and rapid erosion and deposition. The absence of predicted geochemical variations indicates that magnetite and phyllosilicates formed by diagenesis under low-temperature, circumneutral pH, rock-dominated aqueous conditions. Analyses of diagenetic features (including concretions, raised ridges, and fractures) at high spatial resolution indicate that they are composed of iron- and halogen-rich components, magnesium-ironchlorine–rich components, and hydrated calcium sulfates, respectively. Composition of a cross-cutting dike-like feature is consistent with sedimentary intrusion. The geochemistry of these sedimentary rocks provides further evidence for diverse depositional and diagenetic sedimentary environments during the early history of Mars.

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Volatile and Organic Compositions of Sedimentary Rocks in Yellowknife Bay, Gale Crater, Mars

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H₂O, CO₂, SO₂, O₂, H₂, H₂S, HCl, chlorinated hydrocarbons, NO, and other trace gases were evolved during pyrolysis of two mudstone samples acquired by the Curiosity rover at Yellowknife Bay within Gale crater, Mars. H₂O/OHbearing phases included 2:1 phyllosilicate(s), bassanite, akaganeite, and amorphous materials. Thermal decomposition of carbonates and combustion of organic materials are candidate sources for the CO₂. Concurrent evolution of O₂ and chlorinated hydrocarbons suggests the presence of oxychlorine phase(s). Sulfides are likely sources for sulfur-bearing species. Higher abundances of chlorinated hydrocarbons in the mudstone compared with Rocknest windblown materials previously analyzed by Curiosity suggest that indigenous martian or meteoritic organic carbon sources may be preserved in the mudstone; however, the carbon source for the chlorinated hydrocarbons is not definitively of martian origin.

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Mars' Surface Radiation Environment Measured with the Mars Science Laboratory's Curiosity Rover

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The Radiation Assessment Detector (RAD) on the Mars Science Laboratory's Curiosity rover began making detailed measurements of the cosmic ray and energetic particle radiation environment on the surface of Mars on 7 August 2012. We report and discuss measurements of the absorbed dose and dose equivalent from galactic cosmic rays and solar energetic particles on the martian surface for ~300 days of observations during the current solar maximum. These measurements provide insight into the radiation hazards associated with a human mission to the surface of Mars and provide an anchor point with which to model the subsurface radiation environment, with implications for microbial survival times of any possible extant or past life, as well as for the preservation of potential organic biosignatures of the ancient martian environment.

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In Situ Radiometric and **Exposure Age Dating of the Martian Surface**

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We determined radiogenic and cosmogenic noble gases in a mudstone on the floor of Gale crater. A K-Ar age of 4.21 ± 0.35 billion years represents a mixture of detrital and authigenic components and confirms the expected antiquity of rocks comprising the crater rim. Cosmic-ray-produced ³He, ²¹Ne, and ³⁶Ar yield concordant surface exposure ages of 78 ± 30 million years. Surface exposure occurred mainly in the present geomorphic setting rather than during primary erosion and transport. Our observations are consistent with mudstone deposition shortly after the Gale impact or possibly in a later event of rapid erosion and deposition. The mudstone remained buried until recent exposure by wind-driven scarp retreat. Sedimentary rocks exposed by this mechanism may thus offer the best potential for organic biomarker preservation against destruction by cosmic radiation.

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