THE ASTROBIOLOGY OF MARS: METHANE AND OTHER CANDIDATE BIOMARKER GASES, AND RELATED INTERDISCIPLINARY STUDIES ON EARTH AND MARS.

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Introduction: On Mars, the search for life has been a principal goal for centuries, and it remains so today. In pursuit of this objective, we present the results of Strategic Initiative 6, developed at the NAI Workshop in Tempe AZ.

Background: 19th century visual impressions of surface albedo markings (Schiaparelli, Lowell) and their temporal changes were mis-interpreted as "canals" and "seasonal vegetation", fueling the fantasies of many laymen and some writers (e.g., Burroughs, Welles), Such views persisted in some quarters until the mid-20th century, ending only with the advent of Mars exploration from space.

In 1965, Mariner 4 returned images of a heavily cratered Mars that ended the perception of a widely vegetated planet. In 1969, Mariner 7 opened an era of searches for other biosignatures with the announced discovery of methane and ammonia; however, a retraction was issued almost immediately when the detected spectral signatures were assigned instead to CO_2. The Mars-orbiting Mariner 9 characterized the atmosphere in detail (composition, temperature) over several annual cycles, and showed discouraging upper limits of potential biomarker gases, including methane. Mariner 9 and later searches through 2000 (KPNO, ISO, CFHT) were averaged over the dayside hemisphere, and sometimes over all seasons, and they provided a parade of increasingly sensitive searches but no clear detections.

Beginning in 1976, the Viking 1 & 2 orbiters imaged large areas of Mars at high spatial resolution, revealing many landforms that suggested the presence of flowing water on early Mars (>3.5 Ga). The orbiters also explored the global distributions and annual cycles of CO_2 and water, while landed payloads searched for microbial life and extant organics in near-surface soil samples without success. The search for life then shifted to identification and mapping of geomorphology and mineral signatures characteristic of long exposure to water ("Follow the Water"). In 2001, Mars Global Surveyor identified hematite (a mineral that forms in standing water) in Sinus Meridiani, which then was chosen as the landing site for the Opportunity rover. Opportunity confirmed long-standing water but found no evidence of extant biogenic minerals (e.g., carbonates) in near-surface samples. Mars Express (Omega) and Mars Orbiter (CRISM) identified and mapped phyllosilicates in several regions, and (in 2008) carbonates were identified in Nili Fossae by MO (CRISM). [The currently favored landing sites for the Mars Science Laboratory are based on these signatures of early Mars.] Mars Odyssey mapped near-surface hydrogen (water?) over much of the planet and identified several regions where it was enhanced, and near-surface water ice and perchlorates were sampled at a high latitude site (Phoenix lander). Themis searched most of Mars for active volcanoes and for sites showing excess geo-thermal heat, but none was found.

By 2000, new high-resolution infrared echelle spectrometers were commissioned at several ground-based observatories permitting a more sensitive search for trace gases on Mars. Initial work emphasized ozone, CO, and water. A renewed search for methane began in 1999, and emphasized mapping Mars to search for local variations of methane on Mars that might change with season (e.g., polar enhancements in winter). Three active regions were identified at mid-latitudes in Northern summer 2003, described at scientific meetings and published in early 2009 [1] (publication was deferred until revised data analysis algorithms were developed and validated). Two more regions of active release were found in 2005 (mid-spring in the Southern hemisphere) [2]. Simultaneous measurements of water were obtained for each footprint on the planet, providing for the first time detailed maps of these two trace gases on Mars [2]. Mars Express reported methane detection in 2004 with some suggestion of spatial and temporal variation, however the instrumental sensitivity was too low to permit spatial mapping [3,4].

The principal candidates for the origin of Mars methane include abiotic processes such as water-rock reactions, radiolysis of water, and pyrite formation, all of which produce H_2 that could then generate methane and hydrocarbons via Fischer-Tropsch synthesis with CO and CO_2. Pyrite formation releases abundant H_2, while its reaction with anoxic water produces copious peroxide (H_2O_2) and O_2, and could provide an important source of sub-surface oxidants for destruction of methane along with additional oxygen production. Fluid-rock reactions can also generate hydrogen from both alteration of basalt and the serpentinization of ultramafic rocks (peridotites). In either case, the released H_2 can form methane on combination with CO and/or CO_2. Basalt is the predominant rock-type on Mars, but serpentine has been identified in the Syrtis

Major - Nili Fossae region where active release of methane is also found. H_2 has been detected in the Mars atmosphere and was assigned to photolysis of water; it is not known if active geochemical processes also contribute to H_2 production on Mars.

On Earth, serpentinization occurs both beneath the hot (>400°C) and acidic (pH 2-3) magma-hosted hydrothermal systems that produce black smokers, and in the cooler (<100°C) and more alkaline (pH 9-11) hydrothermal systems such as Lost City located off axis on the Mid-Atlantic Ridge or in surface-serpentinizing seeps such as in Oman, California, or the Philippines. Serpentinization involves the reaction of water with olivine, in particular peridotite (`Mg1.6 Fe0.4 SiO4). This reaction is exothermic, produces alkaline fluids and very high concentrations of H_2 (one cubic meter of olivine can produce approximately 500 moles of H_2 during serpentinization) and can result in a 20-40% gain in rock volume, resulting in the uplift of altered material and exposure of fresh peridotite surfaces through brittle fracturing. The H_2 reduces CO_2 to methane and other hydrocarbons (up to C5). The alkaline fluids produced by serpentinization cause the precipitation of CO_2 (dissolved as HCO_3^-) resulting in the formation of large carbonate chimneys at Lost City.

Active chimneys harbor dense biofilms of a single group of methane-cycling Archaea, the Methanosarcinales. At Lost City, these organisms are growing to at least 90°C and at very alkaline pH (the temperature range for growth of methanogens is from <0°C to >110°C). There is also evidence from stable isotope experiments that the Lost City Methanosarcinales is both making methane and oxidizing methane anaerobically. The details of this complex physiology are not completely worked out particularly since at such high pH, there is no dissolved CO_2 in the hydrothermal fluids for biological reduction of CO_2. Seismic measurements indicate that the fluids beneath the Lost City massif penetrate to depths of 500 meters or deeper beneath the seafloor and may reach moderately high temperatures (between 150° to 200°C).

Kimberlite pipes in the Canadian Arctic have a number of important features that make them potential analog sites for investigation of CH_4 sources. Kimberlites contain peridotite that upon hydration and alteration (serpentinization) produces abundant H_2 (so much so that some diamond exploration companies use H_2 as a prospecting tool). Hence the pipes provide an ideal setting to investigate the link between serpentinization and CH_4 (and higher hydrocarbon) production, as well as mechanisms for the escape of gases to the surface due to the fractured nature of the pipe setting. The relevance to Mars is the interaction between water and ultramafic rock to produce products having astrobiological significance, and mechanisms of release of subsurface gases via fractures connecting to the surface. Focusing on a crystalline rock setting allows the examination of diagnostic features for distinguishing between end-member microbial and abiotic CH_4 - producing reactions without the complicating feature of a significant contribution from biological organic matter (recent or ancient) that is inherent in many of the existing permafrost studies in settings overlain by significant sedimentary deposits (e.g., the Alaska North slope).

Arctic analog sites provide the opportunity, among other things, to examine how well we really understand the isotopic fractionation associated with microbial methanogenesis by cold-loving and cold-tolerant organisms. In light of the substantial re-evaluation of fractionation during microbial methanogenesis by thermophiles and under high pressures, re-examining fractionation by cold environment communities is overdue. It is becoming increasingly clear that it may be a challenge to try to extrapolate models of carbon and hydrogen isotope fractionation during microbial methanogenesis (developed largely from shallow marine environments and sedimentary basins in the 1980s and 1990s) to distinctly different environments such as the deep subsurface and/or cryosphere.

Terrestrial volcanoes release mantle-derived methane in small amounts, however, much more SO_2 is released and it has not been found to date on Mars. It is interesting that two methane release sites on Mars are near or over the flanks of ancient volcanoes, while two other sites are not. The fifth site (Nili Fossae) shows evidence for serpentine, carbonates, and phyllosilicates.

These considerations have important implications for several lines of investigation: 1. A wider range of possible geologic settings and rock types beyond just hydrated ultramafics might contribute to abiotic methane production by water-mineral reactions. These can be evaluated through Earth analog investigations and laboratory experiments, 2. Characterizing the isotopic fractionation associated with these reactions (for a range of possible carbon sources) could help distinguish abiogenic from biogenic methane, 3. The patterns of transforming methane to associated gases such as higher hydrocarbons may vary for different reactions and geochemical conditions and may contribute to distinguishing such gases from biogases by compositional ratios.

Thrust: Our suggestions for coordinated interdisciplinary investigations will be presented.

References:

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