

01 Mar 2016

Early Acidification of Mars and the Potential Implications for Biology

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Recommended Citation

S. S. Johnson et al., "Early Acidification of Mars and the Potential Implications for Biology," *Proceedings of the 47th Lunar and Planetary Science Conference (2016, The Woodlands, TX)*, Lunar and Planetary Institute, Mar 2016.

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EARLY ACIDIFICATION OF MARS AND THE POTENTIAL IMPLICATIONS FOR BIOLOGY. S. S. Johnson¹, D. Goerlitz¹, K. C. Benison², M. R. Mormile³, and D. W. Ming⁴. ¹Georgetown University, Washington, DC, sarah.johnson@georgetown.edu, ²Dept. of Geol. and Geography, WVU, Morgantown, WV, ³Dept. of Biol. Sciences, Missouri S&T, Rolla, MO, ⁴NASA Johnson Space Center, Houston, TX.

Introduction: A leading paleoclimate theory for Mars, based on the identification of phyllosilicate minerals in ancient terrains, posits that the first several million years of the planet's history were dominated by neutral to alkaline pH [1]. However, evidence is mounting for the consideration of an alternate hypothesis: that some smectites on Mars formed under acidic conditions, and that the early surface of Mars may not have been subject to circum-neutral pH conditions, at least not uniformly. Work on shergottitic liquids suggests that up to 2400 ppm of sulfur could have degassed from martian magma, supplying more than enough sulfur for the planet's sulfate-rich sediments and sedimentary rocks [2], and isotopic evidence of mass independent fractionation reveals that sulfur in martian meteorites underwent atmospheric reactions [3]. Radiative modeling of sulfur volatiles in the martian atmosphere indicates that SO₂ and H₂S would have acted as powerful greenhouse gases trapping heat in different wavelength-dependent atmospheric windows than CO₂ and H₂O, supplying the necessary heat for surface temperatures to rise above freezing [4]. Photochemistry suggests that sulfur would have been removed from the atmosphere through the deposition of sulfur dioxide, oxidized to sulfate at the surface-atmosphere interface. This, in turn, could have led to the early acidification of the surface [5], thereby explaining the paucity of carbonates on Mars.

This idea is supported by 1) the recent laboratory synthesis of Fe/Mg smectite from an Adirondack basalt simulant in an acidic hydrothermal system [6], and 2) studies of the mineral composition of terrestrial analogs, particularly at acid salt lakes [7-11].

Acid Salt Lakes in Yilgarn Craton: The Yilgarn Craton in Western Australia is one of the only places on Earth that acid salt lakes occur naturally (See Fig 1). The craton is comprised primarily of deeply weathered Archaean rocks; the host rocks include granites, granodiorites, gneisses, anorthosites, quartzites, and ironstones along with some mafic and ultramafic rocks which are present as greenstone belts [9]. Amid this Precambrian bedrock, a regional acid brine groundwater system supplies water to dozens of shallow, ephemeral lakes [10]. Sulfur is thought to be one of the most important elements in this extreme environment, where cycles of flooding, evapoconcentration, and desiccation promote rapid chemical and physical changes [12].

Yet within the lake sediments, a range of phyllosilicates, some of which are authigenic, has been found alongside sulfates [8]. In addition to acid-stable Al-phyllosilicates, Fe/Mg-phyllosilicates have been detected in moderate amounts in multiple lakes, including the $\leq 62\mu\text{m}$ fraction of the sediments of Lake Aerodrome [8] (lake water pH: 2.7–3.7, groundwater pH: 2.5–3.7).

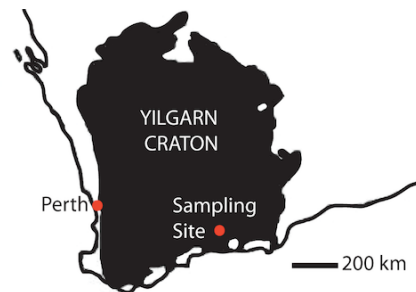


Figure 1: Ephemeral acid salt lakes in Western Australia range from several square meters to several square kilometers in size with pH as low as 1.4 and salinity as high as 32% total dissolved solids.

Biological Potential: In acid salt lakes, organisms must contend tremendous salinity, extreme proton pressure, complex geochemistry, water stress due to desiccation, dramatic diurnal temperature changes, and high levels of solar radiation. These conditions, however, would not necessarily impede the existence of microbial organisms on ancient Mars.

An astonishing diversity of life can be found within acid salt lake waters and sediments [13-15]. In addition to already reported findings, recent next generation sequencing of Lake Aerodrome sediments reveals the presence of over 2500 different species (see Fig 2) in moist sediments collected approximately 3 cm in depth from midlake facies at a time of complete lake desiccation (groundwater pH 3.0, 24% TDS, 25°C).

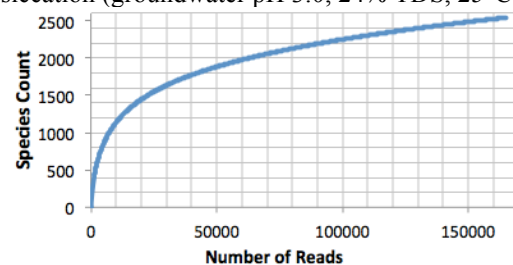


Figure 2: Species count as a function of the number of reads based on paired-end Illumina sequencing (total bp count passing QC: 42,911,678).

The sediments are dominated by *Bacteria* (89.6%),

particularly *Acidobacteriales* (See Fig. 3). Within the *Archaea* (2.9%), are several clades of *Halobacteria*, an extremely halophilic organism that inhabits salt lakes and salterns and can grow on or within salt crystals.

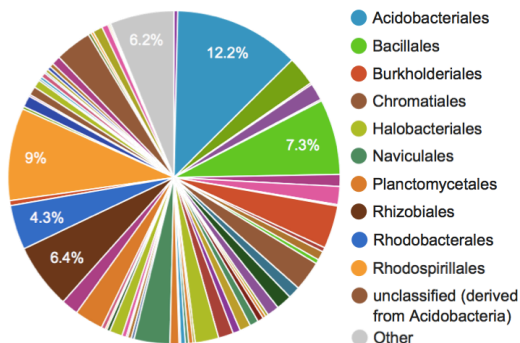


Figure 3: The pie chart illustrates the distribution of taxonomic orders within the Lake Aerodrome sediments; slice size indicates the percentage of reads with predicted proteins and ribosomal RNA genes based on the annotation source databases used by MG-RAST [16].

Interestingly, *Eukaryota* (7.4%) were detected at an even higher level, including *Naviculales*, an order of diatoms, also identified morphologically by scanning electron microscopy amidst gypsum and halite crystals (See Fig. 4). These results mirror the unexpected eukaryotic detections in Spain's highly acidic Rio Tinto, adding credence to the idea that adaptation to low pH and high concentrations of heavy metals may be more easily accomplished than previously thought [17].

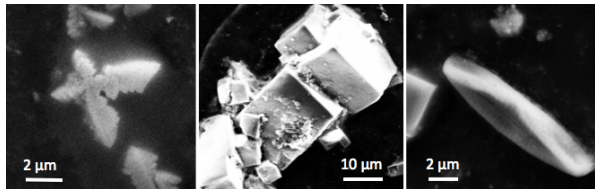


Figure 4: SEM view of gypsum crystals, halite crystals, and the frustule of a diatom.

Implications: Sites of co-located phyllosilicates and hydrated sulfates are particularly compelling places to explore in order to better understand climate history and surface processes on Mars, including southern Meridiani Planum, Columbus Crater, Gale Crater, and Northern Meridiani Terra [7]. The biological potential of terrestrial analogs also makes these sites of great interest for astrobiology.

Despite the challenging conditions at Lake Aerodrome, including extremely high levels of dissolved major ions and elements (up to 73,500 mg/L Na up to 8880 mg/L Mg, up to 601,600 mg/L Cl, up to 8960 mg/L SO₄, up to 376 mg/L K, up to 1780 mg/L Ca, up to 716 mg/L Br, up to 4580 mg/L Si, up to 3274 mg/L Al, up to 196 mg/L Fe, and no detectable HCO₃ [18]),

the surprisingly high level of phylogenetic diversity suggests intriguing possibilities for Mars. Additional work is in progress to understand not only the composition of the community but also energy harvesting pathways utilized by organisms in Lake Aerodrome. The first metagenomic study of an acid salt lake, also located in the Yilgarn Craton, suggests that we may be meaningfully underestimating the effects of biology on the chemistry of these clay- and sulfur-rich environments, in that microbes themselves may be influencing the acidity of these sediments and/or precipitating characteristic minerals as a byproduct of their metabolism [15]. For example, a type of crystalline jarosite that is stable in the presence of water can be formed by *Acidithiobacillus* in both aerobic and anaerobic environments, and thus its detection on Mars, particularly in the context of persistent aqueous processes, may serve as a biomarker for microbial sulfide oxidation [19]. A better understanding of how biology affects patterns of mineralization in these environments is key.

Another question that remain is whether traces of life in these environments have been preserved through time in the geologic record. It is generally believed that the decay of organic matter should rapidly proceed as long as oxidants, such as Fe(III) minerals, remain present in the sedimentary environment, yet organic carbon may be preserved depending on how organic molecules are hosted in mineralogically diverse sediments [20, 21], and preliminary results indicate that lipid biomarkers are surprisingly stable in the depositional environment represented by these lakes [14]. Further research is underway to address the potential of these deposits for biosignature preservation.

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