FIELD OBSERVATIONS AND LAB TESTS OF ACID BRINES: IMPLICATIONS FOR PAST DEPOSITION, DIAGENESIS, EROSION, AND LIFE ON MARS. K. C. Benison[1], B. B. Bowen[1,2], R. M Foster[1], E. A. Jagneicki[1], D. A. LaClair[1], J. Walker[1], M. M. Gonzales[1], M. C. Sirbescu[1], J. J. Student[1], S. L. Story[3], F. E. Oboh-Ikuenobe[3], B. Hong[4], M. R. Mormile[4], M. Storrie-Lombardi[5],and S. S. Johnson[6]

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Introduction: Geochemical and mineralogical data obtained from lithified strata of Mars indicate that acid saline waters once existed on and just below its surface [1-5]. This confirms the interpretations of acid waters on Mars by Burns [6,7] based upon spectral signatures suggestive of jarosite and schwertmannite, as well as the theoretical work of Clark [8]. Acid saline environments on Earth are good analogs for martian lithified strata, especially those at Meridiani Planum [9,10]. In addition, acid brines may have been responsible for the formation of channels and some small craters on Mars [11,12]. We propose that acid brines should be considered possible agents of chemical sedimentation, diagenesis, and sediment transportation and erosion on Mars.

Terrestrial acid saline lake systems are an uncommon, but natural, type of extreme environment.Here we summarize the characteristics of modern acid saline systems in Chile, Western Australia, and Victoria, Australia, and how they compare to martian strata. We also present both physical sedimentology and water-rock interaction experiments involving acid brines. Knowledge of the geology, geochemistry, and microbiology of terrestrial acid saline systems may lead to recommendations for future investigations of Mars and better understanding of its geologic evolution and search for possible past life.

Natural Acid Saline Lake Systems:

Chile. Two acid saline lakes have been discovered in the Andes Mountains of western Chile [13]. Salars Gorbea and Ignorado, at elevations of 4000 m and 4200 m, respectively, are shallow saline lakes surrounded by steep sided alluvial fans of volcanic sediments. Average annual temperature is ~0°C and winds are strong. We found that approximately 30% of the surface of both salars contained shallow (<~2 m deep) ponds actively precipitating gypsum crystals. The remainder of the salars were dry and covered by dunes and sandflats of both reworked and effluorescent salts, including abundant gypsum and sulfur (Fig. 1A, B).

Ponds and shallow groundwaters at Salar Gorbea had pHs of 1.8-3.3 and salinities of ~20-29% TDS throughout most of the salar. The far eastern side of the salar contained neutral waters. At Salar Ignorado, ponds and shallow groundwaters had pH of 4.0-4.7 and the waters were relatively dilute, with salinities of 2-3% TDS.

Figure 1. Natural acid saline lake systems A. pH 1.8 water and gypsum and sulfur at Salar Gorbea in Chile.. B. Dust devil reworking gypsum crystals at Salar Gorbea. Note white gypsum dunes. C. Lake Magic in Western Australia with pH 1.7 yellow water on white halite. D, E. Dead Kangaroo Lake in Western Australia with pH 4.3 during flooding (D) and pH 3.3 near desiccation (E). F. Shallow red acid (pH 4.2) groundwater at Lake Tyrrell, Victoria sandflat.

Microbial evidence was observed at both Chilean salars. At Salar Gorbea, pink crinkly mats exist in the most acidic areas, whereas black mats are associated wih the neutral waters. At Salar Ignorado, we noted green algae on some subaqueous gypsum crystals.

Western Australia. Twenty-one extremely acid saline lakes with pH <4 have been studied on the Yilgarn Craton of southern Western Australia over three field seasons [14] (Fig. 1C-E). Another ~30 nearby lakes were classified as modernately acid, neutral, or moderately alkaline. However, the groundwaters seem to be acid on a regiaonl scale with an average pH of 3.5. The Yilgarn Craton has low topographic relief, is at a low elevation, and is composed of highly weathered Archean igneous and metamorphic rocks of felsic - mafic compositions. This region is arid and moderately windy and air and surface water temperatures range from ~10-50 °C.

The lakes are shallow (<~0.5 m deep) and ephemeral, with flooding, evaporation, and desciccation occurring at daily, seasonal, and/or decadal scales. Lakes are surrounded by sandflats, ephemeral channels, and dunes. Clastic sediments here are quartz and reworked gypsum, much of it with hematite coatings.

The acid lakes precipitate the chemical sediments gypsum, halite, hematite, and kaolinite. Shallow acid groundwaters precipitate gypsum, halite, hematite, jarosite, alunite, and kaolinte as very early diagenetic minerals (Fig. 2). Hematite concretions have been found actively forming both below one of the lakes and in shallow sandflat sediment at another lake.

Extremely acid lake and groundwaters in southern Western Australia are Na-Cl-SO_4-Mg-rich brines (up to 28% TDS) that have variable concentrations of Ca and K, and tend to be highly enriched in Br, Al, Fe, and Si, as well as many heavy metals. These waters also have no detectable bicarbonate, an unusual characteristic for natural oxidized waters.

Preliminary microbiological investigations have been conducted. Field documentation and sampling of microbial suspects included foam at lake shorelines, bubbles outgassing from subaqueous sediments, localized iridescent sheens, and rare algal/bacterial shoreline mats. Petrographic examination of halite and gypsum crystals found inclusions of “hairy blobs”, spiky organic bodies that appear to be clumps of sulfate crystals coated with carbon [15]. Biological analyses of lake and groundwaters by traditional culture and molecular methods suggest that novel genera of Bacteria and Archea live here [16,17]. Despite the acidic, oxidizing conditions, lipid biomarkers from these lacustrine environments are surprisingly well-preserved.

Victoria, Australia. The geochemistry, hydrology, and microbiology of Lake Tyrrell has been well-studied [i.e., 18-20]. These lakes are hosted by gently rolling hills on a thick package of Tertiary and Mesozoic sediments and rocks. The climate is semi-arid. We studied seven saline lakes in northwestern Victoria in southeastern Australia during two field seasons. All of the lakes were moderately acid - neutral (pH 5.0 - 6.9). Localized groundwaters around the shore of Lake Tyrrell were extremely acid (pH 3.0-4.7; Fig. 1F). Halite is the main evaporite mineral in the Victorian lakes. Gypsum crystals form displacively in the sediments. Localized early diagenenetic hematite and jarosite grow in the sediments from acid groundwaters.

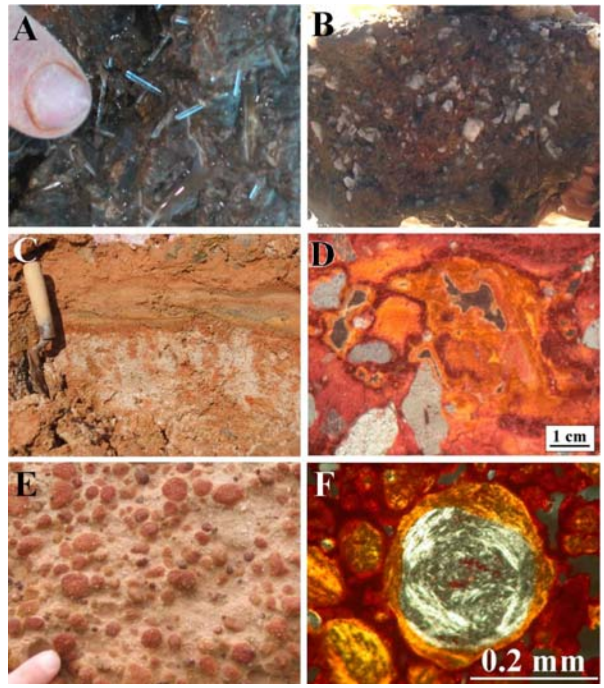

Figure 2. Photographs (all cross-sectional views) of very early diagenetic features associated with Western Australian acid lakes. A. Displacive gypsum crystals. B. Displacive halite crystals. C. Early cements of hematite (red) and jarosite (orange) on sandflat sediment composed of quartz and reworked gypsum. D. Hematite (red) and jarosite (orange) cements in young quartz sandstone. E. Hematite concretions.(D) Interior of single concretion containing ooids of gypsum (replacing halite cube) and quartz grain coated by iron oxides.

Acid Brine Lab Experiments:

Physical Sedimentology Experiments. Physical sedimentology experiments have shown that sulfuric acid solutions and not dilute water may have formed some surface features on Mars. In the laboratory, we ran liquids of various compositions over sediments in order to test how different liquids entrain, transport, and deposit sediments [11]. Dilute water and concentrated sulfuric acid solutions (39% H_2SO_4 and 100% H_2SO_4) produced the same general features, such as channels and alluvial fans. However, sulfuric acid solutions yielded some distinct sedimentary features not produced by dilute water runs. These features, narrow, deeply-incised channels (Fig. 3) and "crater" air bubbles, are similar to some Martian landscape features [12]. In addition, lab tests with cold 39% H_2SO_4 the acid sank below surface level and "tunneled" to create subsurface channel, similar to the underground channels on Mars. For these reasons, acid waters should be considered a possible agent of sediment transport and erosion on Mars. In addition, acid waters took far less time and eroded more sediment than dilute water flow. This suggests that martian channels may have been ephemeral, with flow only occurring over short periods of time.

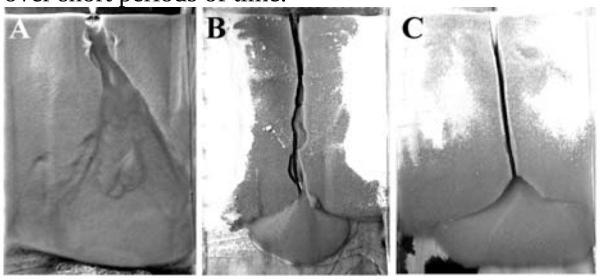

Figure 3. Results of individual physical sedimentology runs. Note entrance hole for liquid at top center of each photo. Bottm of each photo is 18 cm across. Sediment is quartz sand. A. Dilute water run. B. 39% sulfuric acid run. C. 100% sulfuric acid run. In addition, A shows total sediment saturation by water; B and C show partial sediment saturation by acid (dark areas).

Water-Rock and Evaporation Experiments. Water-rock geochemistry experiments were performed in the lab to investigate the role that: (1) various rock types, (2) various water chemistries, and (3) evaporation have on acid brine evolution. Rock samples included gneiss, schist, quartz sandstone, amphibolite, and quartzite collected from three Western Australian acid lakes. Any weathering rinds were trimmed and rocks were weighed, photographed, and put into waters of various chemistries, including deionized water, pH 3.3 H_2SO_4-H_2O, pH 2.2 H_2SO_4-H_2O, and pH 1.6 NaCl-H_2SO_4-H_2O. These three pH values were chosed to reflect the pH range in the natural extremely acid lakes. Periodic measurements of pH, salinity, and air and water temperature were taken.

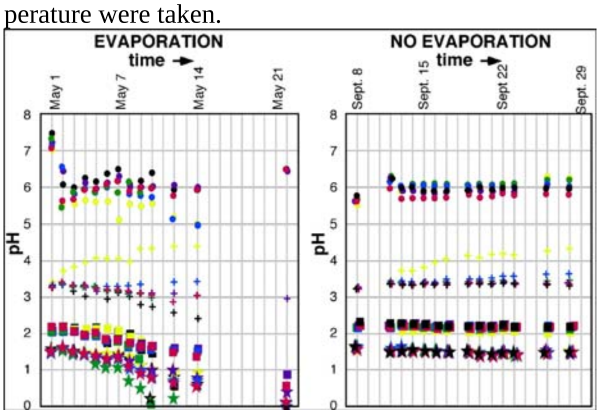

Figure 4. Effect of evaporation, lack of evaporation, and rock type on pH of various solutions. Yellow = sandstone, green = amphibolite, purple = schist, red = quartzite, black = control (no rock).

Results show that evaporation has a greater effect on pH than does water-rock interaction [21]. Acid solutions had decreasing pH over time as evaporation occurred, presumably because the acids were concentrated as water vapor was driven from the solutions (Fig. 4). This matches our field observations, which show that pH fluctuates with flooding and evaporation. The rock type made little difference in this trend of decreasing pH with increasing evaporation. The one exception occurred in the sandstone + pH 3.3 solution (yellow in Fig. 4). Dolomite cement in the sandstone buffered the pH 3.3 acid, but not the pH 2.2 or 1.6 solutions. Of particular interest is the observation that the amphibolite (green in Fig. 4) did not neutralize the acids. Acid solution in amphibolite had decreasing pH over time with evaporation. This supports our field observations of extremely acid brines in direct contact with some mafic rocks.

Comparison with Mars:

Geochemistry and Mineralogy. Of the three modern terrestrial acid brine systems we have studied, the Western Australian systems seem most similar in geochemistry and mineralogy to martian deposits.

Sedimentology. The acid saline settings of Chile, Western Australia, and Victoria, all show some similar sedimentary features as those on Mars. Sediments are primarily sand-sized and include both a siliclciastic component and reworked chemical precipiatates. In-particular, eolian textures are common for the Westen Australian and Chilean sediments. Sedimentary structures in the martian lithfied strata seem to include laminations and thin beds, ripple marks, cross-bedding, and mudcracks. This assemblage of sed. structures also occurs in the terrestrial acid saline deposits, but is more pronounced in the Western Australian depostis than in the Chilean or Victorian sediments.

Diagenetic Features. Two types of distinct diagenetic features, hematite spherulitic concretions and displacive crystal molds have been recognized in the martian lithified strata. Analogous diageentic features have been found in the Australian acid saline lake systems. In Western Australia and in Victoria, displacive gypsum is common (Fig. 2A). In Western Australia, we have found very early diagenetic hematite concretions in at least two specific settings. Semi-soft hematite concretions less than 2900 years old were discovered growing in a sand bed ~20-30 cm below an acid lake bottom. These spherical concretions are 2 mm – 4 cm in diameter and are composed of quartz grains and gypsum and halite ooids coated with hematite (Fig. 2F). One spherical iron oxide concretion was found growing in sand only 1 cm below the sandflat surface adjacent to an acid saline lake. In addition, hematite concretions are abundant throughout Western Australia in recent sandstones that may be paleosols that were formerly lake beds.

In Western Australia, halite, gypsum, hematite, jarosite, alunite, and kaolinite all grow syndepositionally from shallow groundwaters associated with the extremely acid lakes. The diagenetic gypsum and halite occur as displacive crystals. The hematite, jarosite, and alunite most commonly occur as thin grain coatings. In particular, hematite is pervasive at most acid lakes (Fig. 1D,F), but absent at all neutral lakes in

Western Australia. This diagenteic mineral assemblage may be responsible for the similar mineralogy interpreted from the martian lithified strata [1,4].

The Chilean acid salar sediments hosted displacive gypsum, but rare iron oxides. In addition, little jarosite was detected there. In Victoria, small amounts of displacive halite and halite were noted. Hematite and jarosite cements correlated closely, spatially, to localized shallow acid groundwaters and were actively cementing sand on the sandflat surface.

The diagenetic features in Western Australia and Victoria suggest that the similar diagenetic features in martian sedimentary rocks may have formed very early, perhaps during or just after deposition.

Geologic Settings. Of the three terrestrial acid saline settings, it seems as if the Chilean ones have the geologic setting most similar to Mars. Salars Gorbea and Ignorado are situated at 4000 and 4200 m above sea level in intravolcanic basins of high topographic relief. Alluvial fans are composed of volcanic rocks that are reworked by winds. Ventifacts are common.

Despite the apparent similarity in geologic settings, the Chilean deposits do not seem to be close geochemical or mineralogical analogs for Mars. They have rare iron oxides, little jarosite, and no concretions.

Summary. No terrestrial environment is an exact match for Mars. Our work shows that there is variability in the types of acid saline systems, just as there are many different kinds of alkaline saline systems. However, acid saline ephemeral lakes seem to be the most similar terrestrial system to Mars in terms of sedimentology, mineralogy, geochemistry, and diagenesis.

Recommendations for Future Study of Mars:

Better understanding of past environments. Understanding terrestrial acid environments provides a framework for making interpretations about the deposition and evolution of martian environments. Field observations of processes and products occurring on various temporal and spatial scales in modern acid saline lakes, analytical lab work of samples from such environments, and experiments in the lab all have implications for interpreting past environments on Mars.

The astrobiological implications. We propose that terrestrial acid saline systems provide excellent repositories for microfossils. Halite and gypsum grow rapidly and easily trap liquids, solids, and even air. We have observed hematite mud, kaolinite mud, unidentified yellow crystals, anhydrite crystals, silica spherules, insects, pollen, and "hairy blobs" within primary halite and gypsum crystals (Fig. 5). Based upon recent retrievals of bacteria from fluid inclusions in natural and synthetic halites [22,23], it is likely that the fluid inclusions in evaporites from acid systems also contain microorganisms.

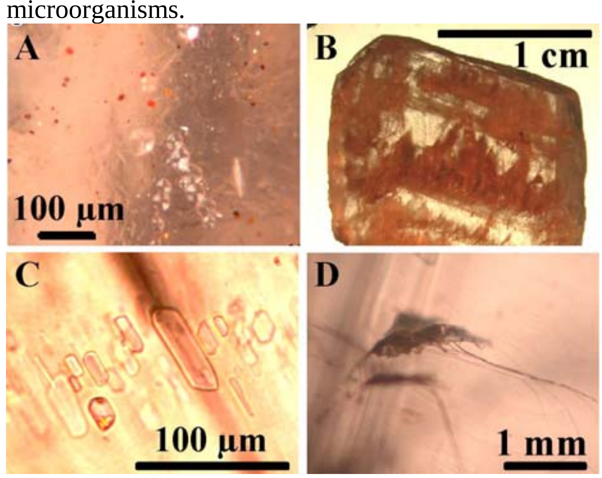

Figure 5. Liquids and solids trapped in minerals from Western Australia. A. Hematite and silica in halite. B. Gypsum crystal with hematite trapped along growth bands. C. Primary fluid inclusions in gypsum, with trapped lake water and tiny yellow crystals. D. Fly in halite.

Halite and gypsum ooids within hematite concretions are protected from dissolution. Some microfossils are covered with a thin layer of hematite, trapped in halite or gypsum, reworked, and later re-enveloped in insoluble hematite. So martian microorganisms may be preserved in the martian rock record. Therefore, any evaporite minerals in hematite concretions on Mars should be targeted for petrographic and geochemical signatures that may indicate past life on Mars.

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