HEMATITE CONCRETIONS FROM MODERN ACID SALINE LAKE SEDIMENTS AS GEOCHEMICAL AND ASTROBIOLOGICAL TOMBS.

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Introduction: Ubiquitous hematite spherules interpreted as being concretions [1] within reworked evaporite dune and interdune lake sediments [2] in the Meridiani Planum region of Mars have revealed a wealth of information about the role of acid saline waters in the planet's past. The variety of processes and conditions that could generate such deposits raises many questions about the formation of mixed iron oxide and evaporite sediments, the potential role of organisms in presumably hostile acid saline systems, and the preservation potential of organisms within this sedimentary record. Sediments from the shallow acid saline lakes in southern Western Australia (Figure 1) provide an important modern analog environment that illustrates potential early and rapid formation of hematite concretion-bearing evaporites, and the excellent astrobiological preservation potential of such deposits.

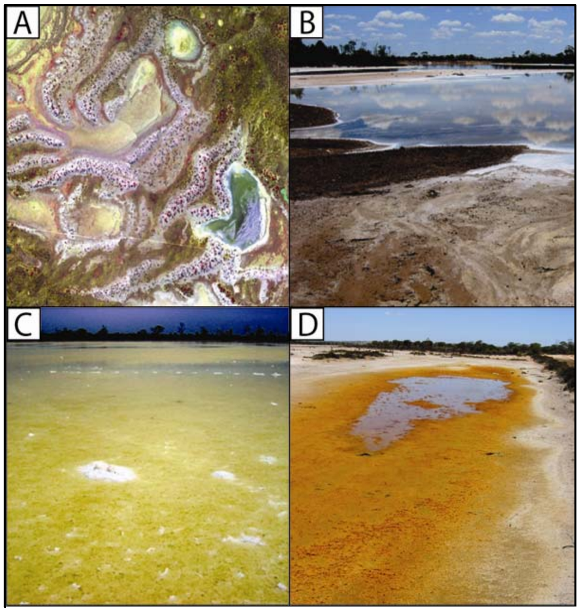

Figure 1. Acid saline lakes in Western Australia. A) False color aerial HyMap image of gypsum dunes surrounding ephemeral lakes [3]. B) Lake Brown- where hematite concretions were found forming in sub-lake sediments. C-D) Two additional acid saline lakes, illustrating the diversity of water color (yes, the water in C is bright yellow and has a pH of 1.7 and 28% salinity) and chemical precipitates in these naturally acidic and evaporative conditions.

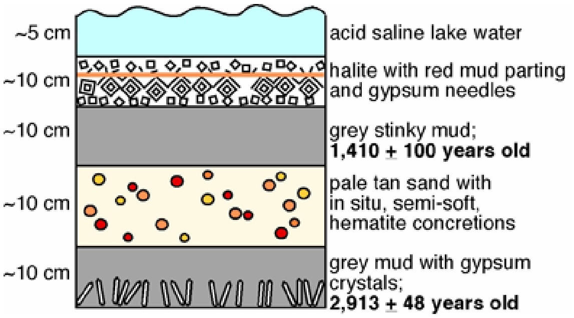

Figure 2. Generalized stratigraphy and ages of reworked eolian and clastic sediments below Lake Brown where hematite concretions are actively precipitating.

Hematite concretions in modern acid saline sediments: Modern interdune acid evaporite lakes in southern Western Australia have sedimetological, mineralogical, and diagenetic features that are somewhat analogous to those observed in the lithified strata in the Meridiani Planum region of Mars [4]. The sediments being deposited within these lakes contain a mixture of clastic and evaporite grains that have been significantly modified by eolian processes [5]. Chemical precipitates from the acid saline surface waters and shallow groundwaters are abundant and include evaporites (halite, gypsum), iron oxides (hematite, goethite), sulfates (jarosite, alunite), and clays (kaolinite, etc.), and continue to be investigated. The sediments also contain thin beds of plant debris that was blown into the lake from the surrounding vegetation, and allows for radiometric ^{14}C dating of the sediments.

Modern early diagenetic spheroidal hematite concretions are actively precipitating in reworked evaporite and siliciclastic subsurface sediments below at least one of these lakes (Figure 2). Semi-soft hematite concretions were discovered in sediments ~30 cm below the lake floor at Lake Brown. The concretions range in size from 2 mm to 4 cm and are composed of isopachous hematite cement that encase host grains composed of reworked evaporite and quartz grains (Figure 3). Lake Brown is a hypersaline (total dissolved solids up to 23%) and acidic (pH ~ 4) ephemeral lake and is one of hundreds of ephemeral saline lakes in the region that range in pH from extremely acid (pH~1.5) to alkaline (pH~10.5) [5]. Shallow

Figure 3. Hematite concretions from acid saline evaporite sediments in Western Australia. Both "hard" and "soft" concretions were somewhat soft in the field, but continued to lithify to differing extents in the lab.

groundwaters saturating the sediments around and below Lake Brown have a pH down to 3.1, and like the surface waters, are highly evaporative and chemically reactive.

Observation of modern iron oxide concretion growth in a natural sedimentary setting provides a rare glimpse of conditions and time scales of formation. The concretion host sediments are between 1400 and 2900 years old, based on radiocarbon dating of stratigraphically lower and higher organic-rich sediments. This indicates that concretions are less than 2900 years old. These absolute age constraints and the observed field conditions (i.e., softness of concretions) suggest that these hematite concretions are actively forming in the modern acid saline environment, and should therefore contain records of the existing geochemical and microbiological conditions. Concretions contain valuable records of diagenetic processes and fluid-sediment interactions, and can also serve as tombs of biological materials that are commonly involved in or just trapped by rapid mineral precipitation processes [6].

The hematite concretions in the Western Australia sediments also provide an example of the geochemical variability that may be expected in chemical precipitates from extreme acid, low temperature, saline fluids. For example, it has been argued that accumulation of trace elements should not be expected in a low temperature sedimentary system and that sedimentary concretions should have a simplistic mineral composition that lack enrichment of unusual trace elements such as Ni [7]. Ni is reported to be enriched in the Meridiani hematite spherules relative to the surrounding sediment [8], which has been used as an argument against a concretionary origin for the Mars spherules [7]. However, similar to the Mars concretions, ancient iron oxide concretions from the Navajo Sandstone in Utah [9], and modern hematite concretions from Western Australia, both show significant enrichment of Ni and other trace elements compared to the surrounding sediments. The Western Australia hematite concretion example illustrates that when fluids involved in concretion growth are acidic or extreme in chemistry, high temperatures, or geologically long time periods are not necessary to enrich the concretions in elements such as Al, Ti, Cr, and Ni [e.g. 10].

The Western Australia acid saline analog environment not only provides an example of hematite concretion formation, but also reveals sedimentological conditions in a setting with active eolian processes in a system where acid saline groundwaters are forming shallow lakes with abundant evaporite and iron oxide precipitation. For example, petrographic observations of the concretions reveal abundant gypsum ooids coated with multiple layers of hematite, presumably from eolian reworking in the presence of acid surface water that was precipitating hematite (Figure 4). Similarities in interpreted depositional conditions (e.g., mixture of evaporative and eolian processes) would suggest that oolitic grains should be expected within the sediments on Mars. The recent discovery of

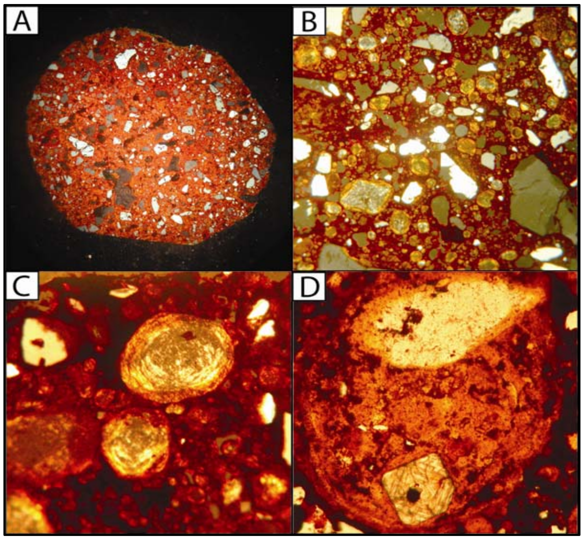

Figure 4. Microscopic views of Western Australia hematite concretions. A) Cross-sectional view of entire 2 cm diameter concretion. B) Mixed reworked evaporite and quartz grains cemented by hematite. For scale, large quartz grain in lower right corner is ~1 mm across. C) Zoomed in on gypsum ooids that are coated by iron oxide. For scale, larger grain is 0.25 mm across. D) Halite (lower cube) and gypsum (upper light grain) encased within hematite ooid. For scale, halite cube is 0.1 mm across. The lines within the halite cube are growth bands composed of primary fluid inclusions.

1 mm size spherules that lack any hematite, could possibly be oolitic evaporite grains.

In Western Australia, early iron oxide grain coatings armor the more soluble evaporite grains and prevent them from dissolving when waters freshen with meteoric input. This iron oxide armor allows the highly labile minerals to coexist with the more insoluble chemical precipitates. The presence of soluble and insoluble mineral phases together and the presence of hematite concretions and evaporite crystal molds on Mars have led to diagenetic interpretations requiring several different diagenetic events over long time periods and involving multiple fluids [10]. However, we have observed these same diagenetic minerals and features forming very early in shallow sediments from the same acid saline groundwater.

Comparisons with other terrestrial hematite concretion analogs: Several terrestrial environments have been identified as being partially analogous based on similarities of sedimentary and diagenetic characteristics. For example, tephra deposits in Hawaii that have been altered by volcanic acid sulfate also contain tiny hematite spherules [11]. The eolian Navajo Sandstone in southern Utah contains abundant spherical iron oxide concretions that precipitated diagenetically at redox fronts [12]. While both of these examples illustrate conditions where hematite concretions can form, they lack the connection with evaporites in acid saline waters. Permian deposits in the central US that contain redbed-hosted evaporites have been interpreted as ancient acid saline lake deposits and also contain spheroidal hematite concretions [13].

While ancient examples provide good outcrop exposures that are similar to the weathering concretion-bearing outcrops on Mars, the subsurface geochemical and sedimentological conditions at the time of formation have to be inferred based on authigenic phases that may have undergone multiple episodes of diagenesis over potentially millions of years. The effects of burial, uplift, erosion, and exposure to surface weathering may complicate interpretations of conditions at the time of formation. Conditions and timing of formation of ancient concretions have been inferred based on interpretations of features such as authigenic mineralogy, host rock properties, and crosscutting relationships. In contrast, the modern hematite concretions from Lake Brown provide an example of early diagenetic hematite concretion formation in acid and saline sedimentological and geochemical conditions that may be analogous to past depositional and early burial conditions on Mars.

Astrobiological implications: Remote spectral data and in situ field data from Mars suggests a history of acid saline waters in the deposition and diagenesis of sedimentary deposits in the Meridiani region. The apparent regional extent of these deposits [14], as well as the existence of additional sulfate-rich deposits in the Gusev Crater region [15], and gypsum dune fields in the northern polar region [16], suggest that the acid saline fluids were likely not constrained to the Meridiani region. The existence of minerals that indicate both acidic and extremely saline fluids on Mars, has pointed to perhaps inhospitable conditions, even if liquid water was once present. However, examination of sediments and fluids in shallow acid saline interdune lakes in southern Western Australia reveals that even these extreme conditions contain traces of a wealth of microbiological biota [17]. Preservation of microfossils in hostile and oxidizing environments such as this has been considered dubious. However, examination of subsurface sediments reveals that in systems rapidly precipitating abundant iron oxides, such as is presumed to have existed in the ancient Meridiani environment, microfossils are commonly trapped. Future missions should consider the importance of petrographic and geochemical inspection of evaporite grains and hematite concretions in the search for possible astrobiological materials.

Conclusion: The hematite concretions forming within the Western Australia sediments provide a model that illustrates the potential for very early, perhaps syndepositional, precipitation of spheroidal iron oxide concretions in reworked evaporite sediments saturated with acidic and saline fluids. Evaluation of microorganism preservation within the rapidly precipitated evaporites and iron oxides in terrestrial acid saline environments suggests the importance of petrographic and geochemical evaluation of such deposits during future missions on Mars.

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