IMPACT OF DIAGENESIS ON BIOSIGNATURE PRESERVATION POTENTIAL IN PLAYA LAKE EVAPORITES OF THE VERDE FORMATION, ARIZONA: IMPLICATIONS FOR MARS EXPLORATION.

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Introduction: NASA's two major priorities for Mars science include (1) seeking biosignatures that can reveal whether Mars hosted life and (2) characterizing the biosignature preservation potential (BPP) of habitable environments [1,2] (i.e., aqueous sedimentary environments such as evaporitic sulfates, including gypsum [3]). This work addresses both priorities with a two-task study of evaporite deposits in the Upper Pliocene Verde Formation in Verde Valley, AZ [4,5]. Evaporites studied include bottom-nucleated halite and displacive growth gypsum in magnesite-rich mudstone. These evaporite lithotypes provide what we consider to be a potentially relevant, but little-studied example of a high priority ancient habitable environment on Mars: Gale Crater.

Goals: The two goals of our study were to (1) identify different evaporite subfacies within the playa sequence and the diagenetic pathways for each and (2) assess how diagenetic processes affected biosignature preservation potential.

Methods: Methods combined outcrop-scale field observations and lab analyses, including: (1) thin-section petrography to understand diagenetic processes and paragenesis; (2) X-ray powder diffraction to obtain bulk mineralogy; (3) Raman spectroscopy to identify and place phases (and kerogenous fossil remains) within a microtextural context; (4) Total Organic Carbon (TOC) analyses to estimate weight percentages of preserved organic carbon for each subfacies endmember; and (5) electron microprobe to create 2D kerogen maps in order to quantify kerogen preservation *in situ* and at the microscale in each subfacies.

Results: Results revealed eight distinct diagenetic histories for each evaporite subfacies and inferred pathways for organic matter preservation. Fine grained sediments (including phyllosilicates) were deposited on ephemeral playas from proximal alluvial fan sources. Evaporative processes formed concentrated brines that accumulated as $CaSO_4$-enriched zones of saturation just below the playa surface. Early diagenetic gypsum grew displacively within the mudstone playa sediments, forming crystal clusters. Gypsum was altered in three diagenetic processes. During periods of lower salinity, displacive growth gypsum dissolved, leaving behind external crystal molds in the host mudstone. In many instances, gypsum crystal clusters were recrystallized. In some instances, molds were infilled with secondary gypsum crystals. Some secondary crystals experienced Na-Ca-Sr cation-substitution, after Na-, Ca-, or Sr-rich brines came into contact with the molds. Gypsum also experienced dehydration to anhydrite, likely when shallow brines reached temperatures of 35°C and pore-fluid salinity reached halite saturation. Another subfacies is represented by haite-thenardite (Na_2SO_4) pods. The pods are interpreted to have formed by localized karsting of older evaporites, forming brine ponds where crystal growth occurred in low areas on the playa surface. This resulted in bottom-nucleated halite (and gypsum) crystallization, followed by later stage thenardite replacement. Ca consumption by sulfate and carbonate precipitation may have lead to progressive enrichment of SO4, Na, and Cl in ponded surface brines. Burial and basin filling, the development of a younger lacustrine lake system dominated by carbonate sedimentation during the Pleistocene, and the cementation of the Verde playa sediments (by magnesite and calcite) were completed by the introduction of Mg and Ca carbonate cements.

Although playa lakes are known to have high rates of organic matter production, diagenesis likely had an impact on biosignature retention following initial capture of organic matter. TOC analyses suggest that post-diagenetic mudstones had the highest BPP. BPP was lower and comparable among displacive growth gypsum and halite-thenardite subunits.

Discussion: These observations help refine taphonomic models for biosignature preservation potential in evaporite environments originating from Mg-Na-Ca-SO_4-Cl brines in hydrologically closed continental basins. This work has the potential to inform *in situ* target identification, sampling strategies, and data interpretations for future Mars Sample Return missions such as NASA's Mars 2020 mission.

References: [1] Committee on the Planetary Science Decadal Survey (2012). National Academies Press, Washington DC. [2] J. Mustard and the *Mars 2020 Science Definition Team* (2013), http://mepag.jpl.nasa.gov/reports/MEP/Mars_2020_SDT_Report_Final.pdf. [3] Schopf, J. W. et al (2012). *Astrobiology*, 12 (7): 1-15. [4] Donchin, J. H. (1983). Doctoral dissertation, NAU. [5] Nations, J. D., et al (1981). *Yavapai County, Arizona: Arizona Geological Society Digest*, *13*, 133-149.