IN-SITU ALTERATION IN SULFATE RICH UNITS OF JEZERO CRATER, MARS.

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Introduction: The Perseverance Rover [1] has examined sedimentary rocks at the delta front within Jezero Crater [2] over the last six months. One unit of particular interest has been informally recognized as the Hogwallow Flats (HWF) member of the Shenandoah formation. The HWF member is composed of approximately 5 vertical meters of light-toned, fractured, platy rocks that alternate in section with mottled, dark-toned rocks, and is similarly expressed in a laterally adjacent unit known as Yori Pass (YP). Both units occur extensively along the delta base in the crater. One possible interpretation for the depositional environment of the HWF member and overlying units of the delta front has been envisaged as part of a sub-aqueous turbidite sequence. This work examines the mineralogy, morphology and geochemistry of targets at HWF and YP and presents a model for the subsequent diagenetic alteration that may have affected these sediments that were deposited in paleolake Jezero.

Methods: We used measurements from SuperCam [3][4], SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals) [5], and PIXL (Planetary Instrument for X-ray Lithochemistry) [6] to evaluate alteration textures and phases at HWF and YP.

Observations: The sedimentary rocks present at HWF are very fine to fine grained sandstones and display clear sub-mm planar laminations with no recognizable cross-lamination. Numerous diagenetic features are present and include spherical and irregular concretions, an Mn rich coating, fractures that appear to resemble desiccation and/or syneresis cracks, and tabular, fracture-filling, anhydrite veins. YP contains siliciclastic rocks composed of uncommon tan granule-sized lithoclasts in a matrix composed of fine sand to medium sand grains. The composition of the lithoclasts is hydrated sulfates. The silt and fine sand is composed of sulfates with lower hydration and phyllosilicates [20]. Furthermore, there are examples of anhydrite granules and nodules in the matrix in addition to anhydrite vein fill. The coarse sandstone unit above HWF is highly enriched in Fe and Mg carbonate whereas the cm-scale laminated unit above YP is phyllosilicate-rich; in both cases, there is a notable absence of sulfates. SuperCam has detected Fe and Mg carbonates to a lower abundance in HWF [7]. The heterogeneous distribution of these alteration phases throughout HWF and YP likely implies multiple episodes of diagenetic alteration, further discussed below.

Model: Based on the sedimentological context, we assumed that deposition involved fluvial transport of fine-grained basaltic grains that subsequently settled out of suspension. Next, we propose that the majority of the alteration phases and textures observed in these units can be explained by chemical transformations in situ by connate waters. The clasts of pyroxene and olivine could have been first cemented by authigenic phyllosilicates and carbonates with ensuing lithification. Long term, low temperature weathering experiments of olivine under a dense CO_2 atmosphere readily produce ferric smectites, Mg carbonate, and a variety of amorphous to weakly crystalline silica phases [8]. This likely occurred during an interval when the delta was still active and represents a phase of circumneutral pH water, presumably at or near the original base level.

The crater then may have begun to lose water over an unconstrained time in the post-Noachian period of Mars history through radiative escape of hydrogen and/or through the formation of hydrated phases, and the retreat of groundwater into the sedimentary basin and underlying crust, which has been shown to

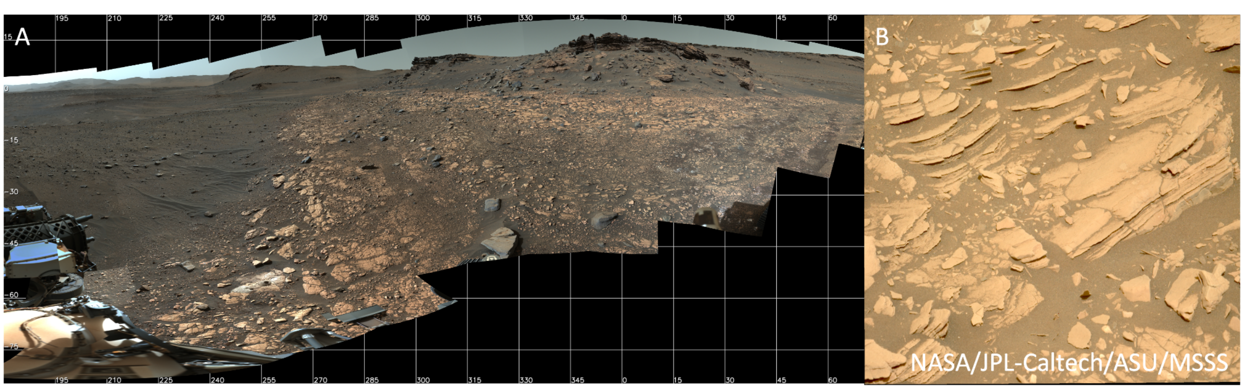

Figure 1. A, *Altered sedimentary rocks at Hogwallow Flats as seen by Mastcam-Z (enhanced color).* ***B,*** *Light-toned, platy, fractured rocks with mm scale planar lamination*

irreversibly consume large amounts of exchangeable atmospheric water [9]. At this stage, the lake level may have decreased to allow for intermittent subaerial exposure of YP and HWF. This may have been accompanied by a change in lake composition towards a sulfate-rich, saturated brine of circumneutral pH. Together, this could have resulted in the authigenic production of Fe/Mg phyllosilicates, sulfate-enriched bedrock, as well as the observed chemical index of alteration (CIA) range ~40-65, all of which are consistent with early diagenetic open-system weathering, and additionally, sulfates of the same Mg # [10] only in the relevant units.

The unit below YP is covered and the unit below HWF (Knob Mountain) may be explained by an igneous intrusion not connected to the delta. Therefore, this sulfate rich brine may have been isolated to a particular elevation as a stratigraphically constrained aquiclude. Sulfate rich brines are also efficient dissolvers of calcium carbonate and to a smaller extent magnesite, which left HWF with a small amount of magnesite and siderite [7] but a largely dissolved flux of mobile Ca2+ ions and smaller amounts of Fe2+ and Mg2+ ions. Experimental studies showed that carbonate dissolution rates are largely unaffected by the saturation state of brines, suggesting likely erasure of carbonate in any type of water [11].

Later on, acidifying conditions, created by ferrolysis and sulfide oxidation, may then have decreased the pH of this solution. Sulfide minerals are commonly found disseminated in Archean age rocks on Earth [12]. Pyrite dissolution rates, on the other hand, decrease significantly in brines, which likely explains the delayed oxidation and acidification of the water from sulfide oxidation [13]. This resulting solution likely precipitated gypsum (when Ca was available), hydrated ferric sulfate phases, and hydrated magnesium sulfate phases, similar to the acid saline lakes of Western Australia [14] [12] in concentrated patches at HWF and YP.

As the lake dried out further, the unit may have been subject to fracturing and sub-aerial exposure; the calcium rich fluid left over could have concentrated in the fractures to create fracture-filled, tabular veins of anhydrite. The last stage of anhydrite precipitation via low temperature, calcium chloride rich brine induced transformation of jarosite [15], is evidenced by the numerous displacive anhydrite crystals and nodules seen in YP. The key to this low temperature anhydrite formation is flowing water instead of stagnant water suggesting a leaching of the bedrock and groundwater movement through these units. Lab experiments of this type of anhydrite formation did not form iron oxides; in addition, flowing groundwater is particularly effective at flushing out nano-scale iron oxides. Both hypotheses could explain the absence of iron oxides in these units. Similarly, studies showed a lack of iron oxide formation in lab tested acid mine drainage, evaporative precipitation sequence [16].

Lastly, late diagenetic sub-aerial exposure of these units could have become oxic enough to produce Mn oxide coatings on bedrock surfaces and/or within fractures. Terrestrial work in Iceland has shown that fractures are efficient at concentrating Mn in basaltic bedrock, which can then oxidize via fluvial or microbial weathering [18]. It is also interesting to note that the targets above YP transition from sulfate and phyllosilicate compositions to pure phyllosilicate composition with elevation, suggesting a putative weathering front of the brine lake.

Implications: The units investigated here have a rich history of diagenesis from neutral high volume of water to neutral pH saturated sulfate brine to acid saturated brine to chloride saturated brine. The model proposed here thus allows for long periods of abundant, neutral pH water at Jezero crater despite the presence of sulfates. Neutral pH lakes are of course rich in microorganisms on Earth; however, saline saturated lakes also are habitable to a large range of microbial life [19] and are able to preserve organics in sulfates and concretions, both of which we see in these units [17]. Furthermore, the sulfate enriched samples of acid saline lakes preserve the highest concentration of organic carbon [14]. Even as the water on Mars was drying up, Jezero could have remained habitable for a much longer period of time.

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