FROM BEDROCK TO DUNES: CLUES ON SILICA DIAGENESIS ON MARS FROM WATER CONTENT AND AMORPHOUS PHASE ANALYSIS.

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Introduction: Diagenetic silica on Mars has been identified globally from orbital data [*e.g.* 1] and in Gusev crater from in-situ measurements by the Spirit rover [*e.g.* 2]. Recently, Curiosity rover observations have suggested the presence of amorphous, high-silica material in altered Gale crater rocks [3,4]. If these deposits are predominantly opal-A [3], they are precipitates of paleo-groundwater on Mars. The presence and degree of maturity of diagenetic silica is thus intimately related to past environmental conditions and can help us understand the habitability of ancient Mars. Recent in-situ analyses of the amorphous component of active dune sands and the hypothesized parent bedrock (shown in Figure 1) allow us to address whether aeolian deposits experience expedited maturation of silica on Mars as suggested by [1].

We report constraints on the abundance of opal-A, among several other amorphous phases, in active dune sands from [5]. Results are compared to those for the hypothesized source bedrock, the Stimson sandstone unit. The presence of ordered forms of silica (opal-CT and quartz) in Gale crater samples are also examined to obtain a larger context for silica diagenesis and alteration conditions.

Methodology: We analyze active neutron die-away from the Dynamic Albedo of Neutrons (DAN) instrument on the Mars Science Laboratory Curiosity rover to estimate the water content of Bagnold dune sands and Stimson sandstone bedrock. We demonstrate that water content can be a useful constraint on the abundance of specific amorphous phases (provided a database of well-characterized amorphous phases synthesized under Martian conditions) [5]. A new Markov-chain Monte Carlo (MCMC) routine for analyzing active neutron spectra has been developed to quantify the correlation of fit parameters and to provide robust quantification of uncertainties [5]. This latest development is a substantial improvement over methods used previously [*e.g.* 4], as it allows for the characterization of correlation between all fit parameters and does not assume a Gaussian-distributed *a posteriori* [*e.g.* 6]. Throughout we utilize a geochemical and mineralogic assay provided by the Alpha Particle X-ray Spectrometer (APXS), Chemistry and Mineralogy (CheMin), and Sample Analysis at Mars (SAM) instruments.

Results at Bagnold dunes: Less than 10% of the water in active dunes in Gale crater is associated with weakly-bound/adsorbed water, as found by SAM [7,8,11]. The dunes also lack hydrated crystalline phases, as determined by CheMin [9]. This dehydrated nature of the dune sands allows us to translate the DAN-derived, best-fit bulk water content for the dunes, 0.68 ± 0.15 wt% water-equivalent hydrogen (WEH), into the adsorbed-free water content of the amorphous fraction specifically [5] (See Figure 2; left). We then generated mixtures of candidate amorphous phases in a Monte Carlo fashion [5] using geochemical constraints [9,10].

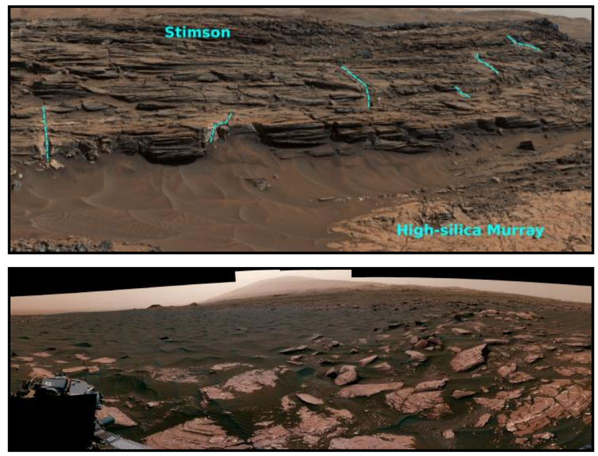

Figure 1 – (Top; sol 993) High-silica fracture halos, mapped as dashed lines, are a non-neglible portion of the Stimson in the Marias Pass region. (Bottom; sol 1647) The Bagnold Dunes location (Ogunquit Beach) where dedicated active DAN measurements were performed on sol 1659. Credit: JPL/NASA/MSSS

In [5] we find opal-A is at least a minor component of the Bagnold sands (~4 wt% of the amorphous fraction), but could represent a larger fraction (up to ~30 wt% of the amorphous fraction). However, models with minimal opal-A content (~4 wt%) necessitate a high-silica glass component that comprises ~15-20% of the amorphous fraction to account for the silica content [5, see Supplementary Material]. All good-fit models necessitate the existence of basaltic glass [5] in Bagnold sands. CheMin indicates the presence of quartz (~0.8-1.6 wt%) and the absence of opal-CT (below CheMin sensing limits) as well [9].

Results at the Stimson sandstone unit: The Stimson sandstone unit, which unconformably overlies the Murray mudstone unit (See Figure 1; top), is a candidate parent source for Bagnold sands [*e.g.* 11]. Both materials are remarkably similar in geochemistry [11] and they have similar amorphous fractions, e.g. 35 ± 15 wt% to 43 ± 16 wt% for Bagnold and 20 ± 15 wt% to 35 ± 15 wt% for unaltered Stimson [9,12]. However, the presence of olivine in Bagnold sands and absence of olivine in the Stimson (below CheMin sensing limits) suggests contribution from another source region (e.g. olivine-rich Gale crater walls) [*e.g.* 11]. Nevertheless, Stimson bedrock remains the primary candidate for Bagnold sands and it is useful to consider our results in this context.

Altered, High-silica Stimson – Stimson sandstone features fracture-associated alteration 'halos' with elevated levels of SiO_2 (~50-67 wt%) and a large amorphous fraction (~65-73 %, uncertainties include larger fractions) [12]. The amorphous fraction contains 64-68 wt% SiO_2. The H_2O and SiO_2 signal from Laser-Induced Breakdown Spectroscopy experiments by the Chemistry & Camera (ChemCam) instrument are correlated and indicate opal-A is a significant component of altered Stimson [3]. High-silica bedrock is also identified in the underlying Murray mudstone unit (see Figure 1; top); the formation of altered Murray and Stimson is suggested to have involved aqueous alteration in one or several stages [12,13].

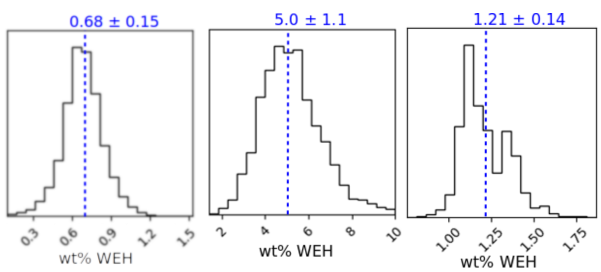

Figure 2 – *A posteriori* likelihood of the water content at Bagnold Dunes (*Ogunquit Beach* target; left), altered Stimson (*Lubango* fracture halo target; middle), and unaltered Stimson (*Okoruso* target; right) from MCMC analysis [5] of active DAN experiments.

We find the altered sandstone is elevated in water content, 5.0 ± 1.1 wt% WEH at the *Lubango* drill target (See Figure 2; middle), consistent with ChemCam estimates [3]. The crystalline fraction of all Stimson drill samples does not contribute significantly to the water content [12]. Considering the amorphous component is predominantly silica, a hydrated silica amorphous phase, potentially opal-A, is likely present in significant abundance. We constrain specific amorphous phases through a similar analysis as [5]. The unaltered Stimson has 1.21 ± 0.14 wt% WEH (See Figure 2; right), indicating a different amorphous phase inventory. Quartz is present in drill samples of unaltered Stimson (~0.4-1.4 wt%) and in altered Stimson (~0.8-0.9 wt%) [12]. Opal-CT was absent (below CheMin sensing limits) in all Stimson targets [12].

Discussion: Stimson sandstone and Bagnold dunes have strikingly similar abundances of quartz and an absence of opal-CT (below CheMin sensing limits). Trace levels of opal-A in Bagnold sands [5] are consistent with the Stimson sandstone unit being the sediment source; eroding Stimson fracture halos would contribute opal-A to the dunes. If Bagnold sands contain elevated levels of opal-A as allowed by [5], it is unlikely that modern martian conditions allow for even slow-acting diagenetic maturation of silica. Interaction of opal-A with water would quickly produce intermediate diagenetic forms (opal-CT) and/or an elevated abundance of quartz [e.g. 14].

[1] suggests aeolian deposits on Mars exhibit more ordered forms of silica, whereas opal-A is predominantly observed in bedrock. Interaction with water in high-latitude glacial environments would allow for the maturation of silica; subsequent global redistribution would then produce equatorial aeolian sediments exhibiting crystalline silica [1]. However, in the case of Gale crater, it is likely that Bagnold dunes consist of material that underwent limited interaction with water, considering the following: 1) the presence of at least minor amounts of opal-A [5], 2) the lack of intermediate forms of diagenetic silica (opal-CT) [e.g. 9], and 3) the presence of a considerable abundance of volcanic glass and olivine [5,9]. Glasses and olivine would have preferentially altered [e.g. 15,16]. Opal-CT is similarly absent in unconsolidated fine-grained deposits (e.g. the *Rocknest* sand shadow) [17]. This is consistent with the lack of evidence for regional sands being delivered to Gale crater from external sources [e.g. 11].

The presence of opal-A in altered Stimson and in at least minor amounts in Bagnold dunes has significant implications for the history of Gale crater. Opal-A readily transitions to more ordered forms of silica in the presence of liquid water. This indicates that minimal, if any, aqueous processes occurred since the formation of high-silica fracture halos.

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