

THE NATURE, CARRIERS AND EXCHANGEABILITY OF VOLATILES IN MARTIAN SOILS: EVIDENCE FOR DISTINCT RESERVOIRS FROM THE BAGNOLD DUNE CAMPAIGN AND OTHER MEASUREMENTS. B.L Ehlmann^{1,2}, B. Sutter^{3,4}, K. Edgett^{4,5}, M. Litvak⁶, C.N. Achilles⁷, N. Thomas¹, W. Rappin¹, A. Cousin⁸, P-Y. Meslin⁸, R. Wiens⁹, A. Vasavada², et al. ¹Div. Geological & Planetary Sciences, California Institute of Technology (ehlmann@caltech.edu), ²Jet Propulsion Laboratory, California Institute of Technology, ³Jacobs Technology, ⁴NASA Johnson Space Center, ⁵Malin Space Science Systems, ⁶Space Research Institute, ⁷Dept. Geosciences, U. Arizona, ⁸IRAP, Toulouse, France, ⁹Los Alamos National Laboratory

Introduction: Orbital mapping shows that martian soils have a ubiquitous 3- μm absorption resulting from OH in mineral lattices, H₂O bound in minerals/mineraloids, and/or H₂O adsorbed on grain surfaces [1-3]. Depending on assumptions about grain sizes, modeling of the IR data predicts minimum abundances of 2-4 wt% H₂O equivalent at equatorial latitudes, up to 6-14 wt% at the polar latitudes. Yet, as pointed out by [4], H₂O measured in situ in both latitude zones was similar, ~1-2 wt%, and smaller than predicted from orbital data. Approximately 1 wt% H₂O was measured by Phoenix in soils above solid ice at 68°N [5,6]. At 4.5°S, 1.5-3 wt. % H₂O was measured by MSL/SAM in the upper centimeters of a sand ripple and 1% in a sand dune [7,8]. The discrepancy may be due to a few molecular layers of water on surfaces and not hydration/hydroxylation of bulk materials. Understanding this discrepancy is important for understanding the amount of water that is sequestered over geologic time in the Mars crust/soils versus exchangeable for modern processes. The quantity available for the latter influences martian volatile cycling, ice volume during periods of different obliquities, and isotopic D/H values.

New data: The Curiosity rover recently collected a suite of data from its instruments [e.g., 7-16] that bear on the question of the quantity and nature of volatiles in martian soils. Most recently, a coordinated set of measurement at the Bagnold dunes allowed characterization of the chemistry and volatile release temperature of distinct size fractions of the soils [e.g., 13]. Coupled with data from prior locations and missions, this allows segregation and description of the properties of distinct reservoirs of volatile-bearing materials. We review the major findings and implications for the volatile content of Mars soils here.

Lack of H, Cl, S volatiles in Bagnold sands: The Bagnold dune sands measured by MSL Curiosity are notable for their distinctly sand-sized particles. Sorting by aeolian transport has led to grain sizes between 50-500 μm and a notable lack of finer grained materials typically comprising a significant proportion of martian soils, including a lack of dust (Fig. 1). Cross-instrument consideration of H₂O, Cl, and S with CCAM, APXS, SAM, and DAN show that the dunes are substantially depleted in these volatiles and enriched in silicates relative to other materials measured

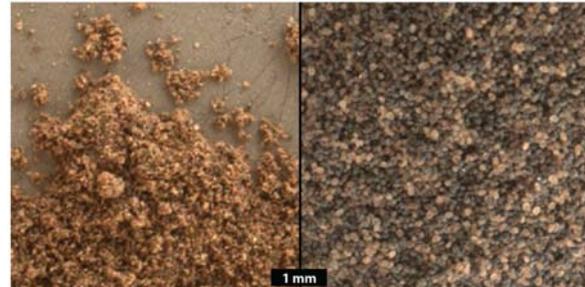


Figure 1. Comparison of grain size of the <150- μm sieved samples from the Rocknest bedform (left) and Namib Dune (right) showing the difference in grain size and dust content.

so far at Gale crater and elsewhere on Mars (Viking, MER, Phoenix).

Lack of detectable water-bearing mineral phases: Anhydrite (CaSO₄) was present but no hydrous crystalline phases were measured in the dunes by CheMin [14], in contrast to numerous rock samples with hydrated/hydroxylated phases. Similar mineralogical data were obtained for the Rocknest location [12], even though this bedform has much finer-grained materials and substantial dust (Fig 1). Thus, any volatile bearing mineral phases present in soils, e.g. phyllosilicates, carbonates, sulfates, nitrates, are present below the ~1 wt% detection limits for CheMin or are poorly crystalline (XRD-amorphous). The amorphous component is 35±15 wt. % of the sand sample [14]

Volatiles in amorphous/poorly crystalline phases: Nevertheless, the Bagnold sands are clearly not volatile free. SAM data show ~1 wt. % release of water vapor from the dune sands at high temperatures. CO₂ (0.9 wt%) and NO₃ (0.03 wt%) release from the <150 μm fraction at the Bagnold dunes are, along with Rocknest, among the highest at Gale crater [Sutter et al., 2016]. The combined use of derived CheMin crystal chemistry [14] with bulk APXS data permits estimation of the composition of this amorphous component(s) and minor phases present at 1% combined: ~50% SiO₂, ~20% FeO, ~10% Al₂O₃, ~5% Na₂O, ~2.5% TiO₂, ~2% CaO, ~1.6% K₂O, and ~0% MgO. The total is only between 85-90 wt. %, consistent with volatile enrichment of the amorphous material.

Different volatiles in different materials – evidence for size sorting of volatile reservoirs: Interestingly, the amorphous component(s) at the Bagnold dunes are quite chemically different in character relative to that cal-

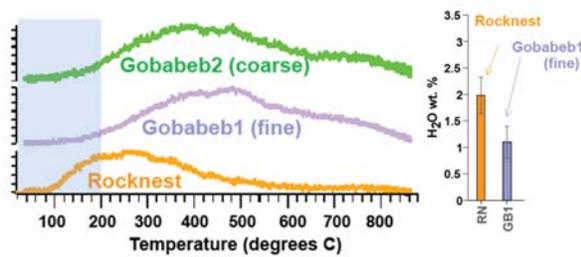


Figure 2. Comparison of H₂O release temperatures and quantities from the dusty Rocknest soil and the Bagnold sand [from 8, 13]

culated for Rocknest. The Rocknest amorphous component has much lower SiO₂ (by 5-20%). Fe, Ti, Ca, Mg, S, Cl, and H₂O are substantially enriched [13-15]. The amorphous component might be poorly crystalline alteration products of the anhydrous minerals detected and/or true glasses (impact, volcanic) that are unusually volatile-rich. The relatively high release temperatures of the water in Gobabeb materials imply it is not likely exchanging with the atmosphere at present but rather formed over geologic time. This is consistent with isotopic data from runs of Rocknest soils at >400°C that are not the same as the modern martian atmospheric average [7]. Thus, we conclude there likely exists a volatile-enriched, Silicate amorphous component with geologic water.

Volatiles in silt- and dust-sized particles: Rocknest, the other aeolian bedform examined in detail with Curiosity's instrument suite has significantly higher H₂O, Cl, and S relative to the Bagnold sands. The principal difference is not mineralogical or in major element chemistry but textural. The Bagnold dunes lack materials <~45-μm in size, the silt and dust-sized fractions, that are present at Rocknest. Thus, chemical and mineralogical data comparing Rocknest with Bagnold, coupled with ChemCam data of dust in the first shots on soil and rock targets [e.g., 9, 10, 16] permit characterizing this finest fraction. ChemCam measurements of dust show lower Si and enhanced H in the first shots of all targets [9]. In contrast to the high temperature releases of water for the sand-sized materials at Bagnold (Fig. 2), approximately ~20% of the water from Rocknest fines is released at low temperatures (<150°C). Isotopic measurements were not made of the lowest temperature H₂O release, but that measured from 230-425°C matches the D/H of the modern martian atmosphere. Thus, at least some portion of the volatiles in the dust- and silt-sized fraction are likely actively exchanging water.

Conclusions and Needed Future Measurements:

We hypothesize that the detailed soil data can be explained by two separate volatile reservoirs in Martian soils. (1) Si-enriched, hydroxylated amorphous phases with H₂O, which dominate the calculated chemistry of

the amorphous fraction for the Bagnold dunes, and (2) Si-poor and Fe-, Ti-, Ca-, Mg-, S, and Cl-enriched dust, which is the source of low temperature water release at Rocknest.

Volatile Reservoir 1 represents a geologic reservoir of water, not likely exchanging currently with the modern atmosphere due to high release temperatures >200°C. Yet, D/H of released water [7] may indicate Amazonian formation rather than being truly ancient. In contrast, Volatile Reservoir 2 in silt- and dust-sized particles has water released at temperatures <150°C. This water can exchange with the atmosphere as relative humidity changes diurnally and seasonally. As such it may be available to participate in the modern-day hydrologic cycle and influence the atmospheric D/H. An implication for human exploration is that Martian fines (particularly <45-μm) may be an easily harvestable resource for water. This is especially true if it can be confirmed that the finest fraction exchanges with the atmosphere at the modern day, possibly permitting dehydration during harvesting then rehydration simply by exposure to the martian atmosphere.

Future measurements can test this hypothesis. Well-calibrated orbital data in the 3-μm region would permit distinguishing the hydrated vs. hydroxylated components, not presently possible given existing orbiting instrument characteristics but important for distinguishing adsorbed vs. mineral/mineraloid bound water. This is also important for understanding the nature of seasonal exchange processes and quantities of water involved. SAM measurements of the isotopic composition of the lowest temperatures of released water at Gale crater may yet be made. Future landed missions might also contain targeted experiments oriented to the volatile content of Martian soils including spectroscopically monitored plates with distinct specific surface areas and spectroscopy of size separates of Martian fines to understand changes in chemistry and chemical bonds with grain size.

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