**THE HYDRATION STATE OF SULFATES ON MARS** Suniti Karunatillake,[1,3] Olivier Gasnault,[2] Scott M. McLennan,[3] A. Deanne Rogers,[3] James. J. Wray,[4] Steven W. Squyres,[5] and William V. Boynton[6], [1]324 Sci&Tech BLDG., Rider University, NJ 08610 (wk43@cornell.edu); [2]Université de Toulouse [UPS], F-31000 Toulouse, France; [3]Stony Brook University, NY 11794; [4]Georgia Institute of Technology, GA 30332; [5]Cornell University, NY 14853; [6]University of Arizona, AZ 85721.

Introduction: The distribution of H_2O on Mars may control any putative extant or extinct biosphere and H_2O activity in the chemical and physical evolution of the Martian surface. Recent identification of sulfates as minerals important to the presence of chemically bound H_2O both by in situ[1,2] and orbital[3] missions motivates the search for spatial patterns to the stoichiometric H_2O : S molar ratio, which we denote as "hydration state" for brevity.

We assess the implications to this topic from the Mars Odyssey Gamma Ray Spectrometer (GRS) derived H_2O and S mass fraction distributions in the mid-latitudinal subsurface at decimeter depths.

Methods: We consider hydration states between 10th and 90th percentiles (Fig 1, yellow) to typify the Martian midlatitudes. This we compare with a com-
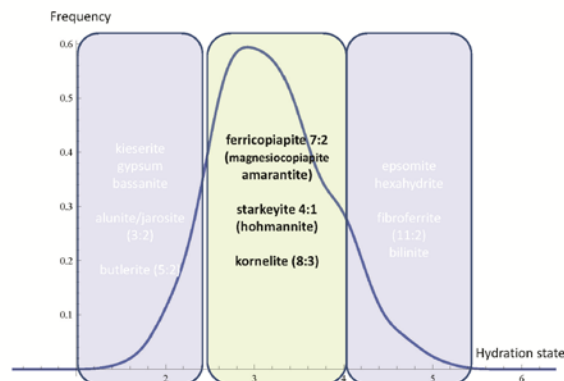
Figure 1 Frequency histogram of hydration states in the mid-latitudes smoothed with a Gaussian kernel. The bulk of the hydration states highlighted yellow are between 2.5 and 4, areally representing approximately 77% of the subsurface.

prehensive mineral library of 27 candidate sulfates representing 13 distinct hydration states that may reasonably be expected on Mars according to 21 papers on orbiter data, in situ data,[4] thermodynamic models,[5] climate models,[6] SNC data,[7] and fundamental research.[8]

The strength of hemispheric and global correlation between mass fractions, w(H_2O) and w(S), constrains the proportion and likelihood of hydrous sulfates. Regression intercepts augment the hydration state picture by indicating whether hydration alone or a mix of an-

hydrous and hydrous phases may dominate. Symbolically, we denote the bivariate correlation coefficient as r, the linear regression as w(H2O) = m×w(S) + C, and the corresponding coefficient of determination as R^2 (Fig 2).

We also identify any latitudinal trends in the hydration state. Optimizing between spatial precision and numerical uncertainty, we use 10° wide latitudinal bands northward and southward of ±10° with a 20° wide equatorial band from -10° to 10° as a reference.
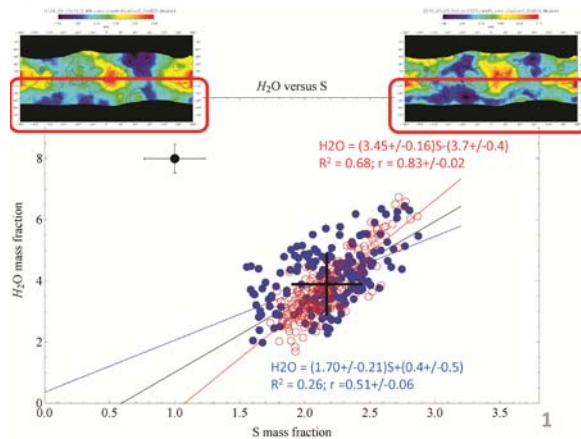
Results: H_2O and S are weakly correlated, the regression intercept straddles zero (Fig 2), and hydration states increase with latitude in the Northern hemisphere. Accordingly, the bulk of sulfates may be hydrated heterogeneously in the north.

In contrast, strong correlation, a positive sulfur intercept at nearly 50% the global average, and hydration states that decrease with latitude characterize the south. The intercept suggests mostly anhydrous sulfates; of the rest, less variable hydration states than the northern counterparts may explain the strong correlation. Furthermore, H_2O intercepts never exceed 15% of average H_2O mass fraction in either hemisphere and ~68% of H_2O variability is attributable to sulfates in the south (Fig 2).

Discussion: Consequently, we propose that climate and subsurface conditions[9-11] in the Martian midlatitudes have inhibited net hydration of sulfates and sustained heterogeneous hydration states[cf., 12] while binding most H_2O to sulfates. Accordingly, abundance of H_2O affects the degree of sulfate hydration more than the S content. Perhaps low temperatures slow the kinetics of otherwise thermodynamically unstable mixtures.[12,13]

Are any hydrous sulfates proposed on Mars consistent with regional scale subsurface observations of hydration states? In our library of candidates, Mg/Ca-sulfates[3,4,14-16] are lacking in the likely hydration states bound between (5:2, 4:1] (Fig. 1 yellow), even though many stable Fe-sulfates exist. Examples include ferri-copiapite, amarentite, hohmannite, and copiapite.

Most important, minerals locally common in the visible and near infrared (VNIR) spectral observations -- kieserite,[3] epsomite,[15] hexahydrite,[4] gypsum,[14,16] etc. -- must occur as mixtures of low and high hydration if they were to dominate the composition.

10.1038/ngeo831 [12] Roach, L.H. *et al. JGR* **114**, E00D02 (2009) doi 10.1029/2008JE003245 [13] Rice, M.S. *et al. JGR* **116**, E00F14 (2011) doi 10.1029/2010JE003683 [14] Horgan, B. *et al. JGR* **114**, E01005 (2009) doi 10.1029/2008JE003187 [15] Feldman, W.C. *et al. GRL* **31**, L16702 (2004) doi 10.1029/2004GL020181 [16] Wray, J.J. et al.. *Geology* **37**, 1043-1046 (2009) doi 10.1130/G30331A.1

Figure 2 Regression in the northern hemisphere (blue) compared to the south (red). South outlined in red in sketches of the H2O (right) and S (left) maps with higher concentrations in reddish hue and lower values bluish. Error bars on upper left show typical uncertainty of data. Cross in the center shows variability of the two distributions. Line fit, coefficient of determination, and correlation coefficient in each hemisphere given to one standard error.

Differences between the GRS observations and VNIR counterparts may be driven by compositional layering deeper than the 10^2 µm depths sampled by VNIR observations, by different minerals dominating at regional scales than local scales, or a combination of both. We expect the MSL rover to constrain these possibilities further with greater depth sampling and longer traverse capabilities.

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