

LATITUDINAL VARIATION IN THE ASSOCIATION OF H₂O WITH SULFUR IN MARTIAN SOIL.

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Introduction: The significance of H₂O to any putative extant or extinct biosphere, as well as its potential role in the chemical and physical evolution of the Martian crust both present and past [1,2] make factors affecting the distribution of H₂O on Mars singularly important. S variation plays an equally important role as a control on inferred fluid pH, alteration environments, and water activity [3]; atmospheric-regolith S cycles and processes may dominate over epochal time scales [4,5]; analogous environments on Earth suggest atmospheric controls on S-cycles [6].

The variability of hydration due to thermodynamic stability [7,8], due to diversity of sulfate minerals as determined remotely [9], and due to diversity observed in situ [10] may obscure any association between H₂O and S. Additionally, ice tables detected within ~ 1 m depth at latitudes as low as 45° [11] suggest a complex interplay among scattered ice bodies at depth and various water-bearing material at shallower levels including clay, zeolite, and silica [12 – 14]. The Mars Odyssey Gamma Ray Spectrometer (GRS) is sensitive to such depth variation as it samples the surface to several decimeter depths. Relative to the tens of microns sensitivity of visible, near infrared, and thermal infrared (VN/TIR) instruments, this may reveal compositional differences with the surface. Such possibility also arises from in situ observations at Gusev Crater where Paso Robles type soil, rich in Fe-sulfates, sometimes underlies “typical” Martian basaltic soil [10]. In the context of such complexities, our recent work [15] suggests a compelling association of H₂O and S, consistent with hydrous Fe³⁺ sulfate distribution at global scales, especially in the Southern hemisphere.

Regolith at grain sizes smaller than gravel, constituting the bulk of the Martian subsurface at regional scales, may be a primary repository of chemical alteration, mechanical alteration, and bio-signatures. The GRS, with hundreds of km lateral resolution and compositional sensitivity to decimeter depth, provides unique insight into this component of the regolith, which we call soil.

In this work, we assess the latitudinal variation in hydration state, as represented by the H₂O : S molar ratio. The latter may contribute to meaningful differences in climate conditions that control the atmosphere-sur-

face interface and resultant soil composition. The regional scope of our work is assisted in particular by the GRS’s intrinsic spatial resolution of roughly 440 km [16], complementing the local chemistry [13] of VN/TIR remote sensing missions.

Data and methods: We use elemental mass fraction data derived from GRS γ photon spectra as discussed by Boynton et al. [17]. These data are limited to between roughly $\pm 60^\circ$ latitude since [17] accurate mass fractions are difficult to calculate within the polar regions with the exception of H₂O. While the relatively low intensity of characteristic peaks for S makes the mass fraction map difficult to generate, spectra accumulated during science operations enabled the first such midlatitudinal map to be created [18]. Nevertheless, substantial smoothing necessary to achieve sufficient numerical precision causes spatial autocorrelation [19] and limits the spatial resolution of the S mass fraction map. Therefore, we utilized $10^\circ \times 10^\circ$ bins for the S mass fraction, $w(S)$, dataset. Accordingly, we binned $w(H_2O)$ from its original $5^\circ \times 5^\circ$ resolution to $10^\circ \times 10^\circ$.

We map the global hydration state distribution by first computing the moles of H₂O, $n(H_2O)$, and of S, $n(S)$, in 100 g of soil at each $10^\circ \times 10^\circ$ bin. This takes the form $w(H_2O) \times 0.0555$ employing standard atomic mass values [20]. Similarly, $w(S) \times 0.0312$ yields the S moles. The molar ratio is computed subsequently, with corresponding uncertainty propagated as

$$\frac{n(H_2O)}{n(S)} \sqrt{\left[\frac{\sigma_m\{w(S)\}}{w(S)}\right]^2 + \left[\frac{\sigma_m\{w(H_2O)\}}{w(H_2O)}\right]^2},$$

where σ_m denotes the standard error of each variable. Ratios in the radical employ mass fractions, since the molar conversion factor for mass fraction and its standard error cancels. The molar ratio and corresponding uncertainty maps underpin our analyses.

We developed a comparative mineral library on the basis of peer-reviewed literature on remote sensing and in situ observations [10,21]; thermodynamic [22] and climatic models [4]; hydration-dehydration experiments that simulate Martian conditions [23]; and meteoritic observations [24]. This places candidate minerals in several overlapping categories: bulk soil observed in situ; outcrop and bedrock sensed remotely or in situ; and thermodynamic feasibility. The nature of γ photon spectra reflecting elemental composition at regional

scale makes the judicious selection of minerals essential; a merely exhaustive list of all terrestrial and laboratory minerals would undermine effective modeling. Accordingly, we consider 27 candidates with 13 distinct H₂O : S molar ratios to compare with the distribution of GRS-derived values.

Results and discussion: Despite substantial overlap in possible hydration states across the mineral groups, Mg-sulfates are generally not hydrated in the 2.5 to 4 range with the exception of starkeyite at 4 [22]; even amorphous meta-stable forms of Mg-sulfates may not exceed a hydration state of 3 [25] and are thermodynamically more likely to be hydrated at 1 – 2 [22].

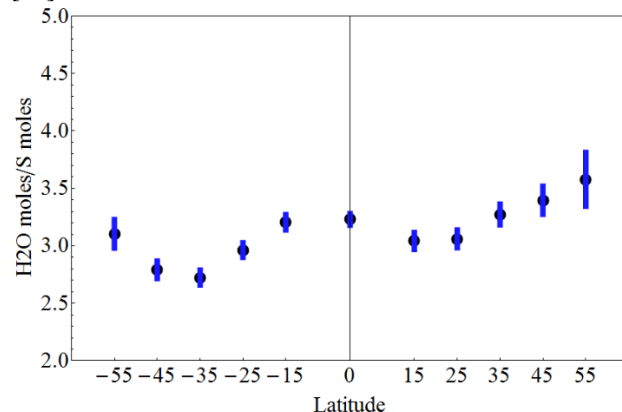


Figure 1. Hydration state plotted against latitude to identify latitudinal variations in average hydration. Blue error bars signify one standard error and the black dot indicates the average, both accounting for heteroscedasticity [26]. Mid-point of each 10°-wide latitudinal bands is shown on the x-axis.

Intriguingly, Figure 1 shows a sustained trend of increasing hydration state from less than 3.5 (e.g., between ferricopiapite and kornelite) to values exceeding 3.5 (e.g., starkeyite) within the map bounds in the Northern hemisphere. Decreasing mean S concentrations accompany this trend. The proportional decrease in average S molar content (moles per 100 g of regolith), of ~16% relative to the equatorial band's 0.074 value (equivalent to mass fraction $.074 \times 32.065 = 2.4\%$), compares favorably with the ~15% proportional increase in the hydration state from ~3.3 at the equator. This suggests less variability in H₂O concentration northward than S, reinforcing the hemispheric-scale decoupling between them in the North [15].

H₂O abundances may decouple from S in the North due to a confluence of decreasing depth to ground ice stability, H₂O accumulation in pore spaces of fine particle mantles presumably thickening northward, H₂O adsorption on fine particles, and specific surface area [27,28]. Additional potential contributors include the proportion of amorphous phases that may adsorb H₂O

[29], weakening chemical association with S. Consequently, sulfate may exert only a minor influence on the latitudinal variations in hydration states in the Northern hemisphere.

Unlike the North, hydration state generally decreases Southward from the Equator (Figure 1). With the exception of the 50° - 60° latitudinal band, the hydration state decreases from the equatorial band to about 2.8 as S molar content decreases to ~0.06. The similar decrease of both by about 15% reinforces the compelling possibility of H₂O bound primarily in sulfates in the Southern hemisphere [15] producing a spatially associated variation in both. Higher hydration state in the 50° - 60° South band relative to much of the Southern hemisphere may reflect a decoupling of S and H₂O in the polar regime of Mars, perhaps analogous to the broader trend at play in the Northern hemisphere.

References:[1] Bishop, J. L. *et al. Planet. Space Sci.* **86**, 130 – 149 (2013); [2] Michalski, J. R. *et al. Nat. Geosci.* **6**, 133–138 (2013); [3] Tosca, N. J. *et al. Science* **320**, 1204–1207 (2008); [4] Halevy, I. *et al. Science* **318**, 1903–7 (2007); [5] Halevy, I. & Schrag, D. P. *Geophys. Res. Lett.* **36**, L23201 (2009); [6] Peng, Y. *et al.* in *44th LPSC* 2427 (2013); [7] Feldman, W. C. *et al. J. Geophys. Res.* **110**, E11009 (2005); [8] Steiger, M. *et al. Geochim. Cosmochim. Acta* **75**, 3600–3626 (2011); [9] Murchie, S. L. *et al. J. Geophys. Res.* **114**, E00D06 (2009); [10] Yen, A. S. *et al. J. Geophys. Res.* **113**, E06S10 (2008); [11] Byrne, S. *et al. Science* **325**, 1674–6 (2009); [12] Jouglet, D. *et al. J. Geophys. Res.* **112**, E08S06 (2007); [13] Bishop, J. L. *et al. J. Geophys. Res.* **114**, E00D09 (2009); [14] Wray, J. J. *et al. Geology* **37**, 1043–1046 (2009); [15] Karunatillake, S. *et al. Geophys. Res. Lett.* **41**, 7987–7996 (2014); [16] Karunatillake, S. *et al. J. Geophys. Res.* **112**, E08S90 (2007); [17] Boynton, W. V. *et al. J. Geophys. Res.* **112**, 1–15 (2007) [18] King, P. L. & McLennan, S. M. *Elements* **6**, 107–112 (2010); [19] Karunatillake, S. *et al. Earth. Moon. Planets* **108**, 253 – 273 (2012); [20] Wieser, M. E. *Pure Appl. Chem.* **78**, 2051–2066 (2006); [21] Lane, M. D. *et al. Am. Mineral.* (2014) doi:10.2138/am.2014.4762; [22] Steiger, M. *et al. Geochim. Cosmochim. Acta* **75**, 3600–3626 (2011); [23] Xu, W. & Parise, J. B. *Am. Mineral.* **97**, 378–383 (2012); [24] Righter, K. *et al. Earth Planet. Sci. Lett.* **288**, 235–243 (2009); [25] Wang, A. *et al. J. Geophys. Res.* **114**, E04010 (2009); [26] Karunatillake, S. *et al. Earth. Moon. Planets* **108**, 253 – 273 (2012); [27] Janchen, J. & Brettschneider, T. in *42nd LPSC* **2**, 1369 (2011); [28] Beck, P., Pommerol, A., Schmitt, B. & Brissaud, O. *J. Geophys. Res.* **115**, E10011 (2010); [29] Meslin, P.-Y. *et al. Science* **341**, 1238670–1238670 (2013).