# SEQUESTRATION OF VOLATILES IN THE MARTIAN CRUST THROUGH HYDRATED MINERALS: A SIGNIFICANT PLANETARY RESERVOIR OF WATER

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**Introduction and Science Objectives:** Estimates of water stored in reservoirs on Mars are typically expressed as the equivalent thickness of water spread over the planet in meters, or a Global Equivalent Layer (GEL). Geological and geomorphological estimates for the total amount of water that may have been present on or passed over the the martian surface, or that resides in the crust, define a minimum of 600 m and range upwards of 3000 m GEL [1, 2], while accretion models suggest a total water inventory of 600-2600 m GEL [3]. Current defined water reservoirs include the north polar cap (5 m [4]), south polar cap and layered deposits (11 m [5]), the cryosphere poleward of 60° (5.5 m [6]), and atmospheric water vapor (10 µm). Significant water may be stored in hypothesized deep aquifers [7], but there has been no evidence for aquifers detected with radar sounding and thus their presence or possible characteristics remain poorly constrained.

Currently defined water reservoirs are insufficient to account for the estimated water inventory for the planet. Water has likely been lost through processes such as impact erosion or solar wind sputtering, and maybe as much as 99% of the original inventory [8]. Observations of globally distributed hydrated minerals (e.g., clays and sulfates) [9, 10, 11, 12] now make it possible to derive a first order estimate of the amount of water that may be stored in the martian crust in the form of hydrous minerals [13]. Here we examine data from the recent Mars missions to accomplish this goal.

Our approach is to estimate the water content of surface soils, characterize the distribution of hydrated minerals across the surface and with depth, and estimate the abundance of hydrated minerals. We then calculate the global average water content of martian rocks and soils to arrive at an estimate of the total amount of water sequestered in hydrated phases.

**Water in surface soils:** Every near infrared spectrum of Mars acquired since the first telescopic IR observations [14] shows clear evidence for the presence of water. Its presence is indicated by a key absorption near 3 µm due to fundamental OH and $H_2O$ stretching vibrations, and Milliken [15, 16, 17] showed that the absolute water content of many hydrous phases can be estimated within ±1 wt. % using this absorption. The strength of this absorption was mapped across Mars with OMEGA data by Jouglet et al. [18], and Millken et al. [17] estimated surfaces to have 2-4 wt. % $H_20$ at equatorial and mid-latitudes. However, certain areas with hydrous minerals (e.g., Mawrth Vallis and Nili Fossae) were enriched in water by 2-3x this amount. High latitude surfaces (polarwards 60°) exhibited water contents up to ~15 wt. %. The global estimates from spectroscopy are broadly consistent with the determination of water equivalent hydrogen (WEH) in the upper ~1 m generated from Mars Odyssey Gamma Ray Spectrometer data [6], which show ~1-3% WEH in most equatorial to mid-latitude zones.

**Distribution of aqueous minerals:** In addition to hydrous phases observed in martian meteorites [19], the diversity of hydrous minerals that have been positively identified on Mars from orbit encompass phyllosilicates [9, 10], sulfates [20, 21], hydrated silica [22], halides [23] and iron oxy-hydroxides such as goethite [24, 21, 25]. These minerals are found in a variety of depositional environments on Mars.

Orbital observations show hydrated minerals occur throughout Noachian-aged terrain [26, 12] and also in crustal materials excavated from beneath Hesperian ridges plains in the northern lowlands [11]. Hydrous minerals are rarely observed in Hesperian or younger terrains [e.g. 27, 28, 22]. Notable concentrations of aqueous minerals are observed in the very well exposed terrains in Nili Fossae [29, 30], Mawrth Valles, Meridiani [20] and Valles Marineris [20, 31, 32]. The detection of hydrous minerals in the crust is biased by exposure; dust and other surficial deposits can obscure the spectral signatures of the bedrock. Therefore, the mapped occurrences of such deposits likely represent a lower limit. Regardless it is clear that hydrous minerals are globally distributed in a diversity of terrains.

**Depth of Alteration:** To what depth in the crust are hydrated minerals observed? Some of the thickest sections of crust exposed on Mars are the walls of Valles Marineris, and phyllosilicates have been observed in exposures of bedrock at the base of the walls of the canyon [10, 33]. These locations are up to 8 km below the plateaus. Impact craters also provide a means to explore the deeper crust of Mars, and a survey of phyllosilicates exposed by impact craters in Terra Tyrrhena showed that craters up to 100 km in diameter contain phyllosilicates in their ejecta or excavated deposits [34], indicating an excavation depth of 10 km. Together, these observations suggest that at least the upper 10 km of crust contain hydrated minerals.

**Abundance of Aqueous Minerals:** Phyllosilicate abundances of various deposits have been estimated using radiative transfer modeling of OMEGA spectra by [35]. Except for Mawrth Vallis where more than 50% phyllosilicate is estimated, the modal mineralogy is dominated by primary non-altered minerals, with minor fractions of phyllosilicates (<30 Vol. %). Current work is focused on determining abundances with CRISM data. Combining estimates of $H_2O$ abundance with maps of aqueous mineral distributions, we conservatively estimate the abundance of hydrated minerals in Noachian crust to range from 1-10% when averaged over all Noachian terrains.

**Translating aqueous mineral abundance to water content:** The water content of phyllosilicate minerals typically averages 12-14% by weight. For the region with the highest phyllosilicate abundance (50% in Mawrth Valles) this would thus result in 7.8-9.1 % water assuming all the non-clay components are anhydrous. The $H_2O$ content of Mawrth Valles region was estimated by Milliken et al. [2007] to be 6-8%, consistent with the clay abudance estimates of water content. Another method to estimate the water content is from terrestrial analyses of altered crust. Altered oceanic crust that typically contains 10% hydrous minerals exhibits an average of 1-3% water [36].

**Table 1**

| Wt % $H_2O$ | Thickness of Altered Crust | Global Equivalent Layer of Water |
|---|---|---|
| 1% | 5 km | 150 m |
| | 10 km | 300 m |
| | 20 km | 600 m |
| 3% | 5 km | 450 m |
| | 10 km | 900 m |
| | 20 km | 1800 m |

**Size of the Hydrous Mineral Crust Reservoir:** Based on the presence of hydrated minerals throughout Noachian aged terrains and the depth to which they are observed, we can estimate the size of the crustal reservoir for water in hydrous minerals (Table 1). We develop these estimates for two ranges. The lower range is for an average water content of 1% and the upper range for 3%. We then consider if the aqueous minerals are distributed over 5, 10, and 20 km of the martian crust. The minerals could be distributed over this range as a consequence of where the original hydrous minerals were formed, such as by alteration in the shallow crust [12], or they could have formed at or near the surface and have been redistributed by burial, impact processes, and/or other sedimentary transport processes. These calculations result in GEL of water from 150 m at the lower end of the estimates to 1800 m for the upper range.

The lower range represents the volume of water that Andrews-Hanna and Lewis [37] estimate would need to have been removed from the active hydrological system to have changed the hydrology of early Mars from one with abundant surface activity (e.g. valley networks) to one dominated by groundwater processes. The upper range would accommodate the total water budget for the planet estimated by some recent models [3]. Regardless, a significant fraction of this 'water' may represent a reservoir that is largely sequestered from participating in hydrological processes unless liberated by impact or heating from volcanism (e.g., structural OH in phyllosilicates). The calculations assume an average water content that is uniform with depth. If the water content instead varies with depth, as is likely, the reservoir size could be enhanced or diminished. Did the alteration of the crust happen slowly leading to a declining abundance of free water? Was this related to the Noachian-Hesperian transition? How did this affect the atmosphere? We will be refining our analyses factoring in new calculations and evaluating the implications for planetary evolution.

**References:** [1] Carr, M. H. (1996) *Water on Mars*, Oxford Univ. Press, New York. [2] Baker, V. R. (2001) *Nature, 412*, 228-236. [3] Lunine, et al. (2003) *Icarus, 165*, 1-8. [4] Phillips, R. J., et al. (2008) *Science, 320*, 1182-1185. [5] Plaut, J. J., et al (2007) *Science, 316*, 92-95. [6] Feldman, W. C., et al. (2004) *JGR Planets, 109, E09006,*doi: 10.1029/2003JE002160. [7] Clifford, S. M. (1993) *JGR Planets, 98*, 10,973-11,016. [8] Brain, D. A. and Jakosky, B. M. (1998) *JGR Planets, 103*, 22,689-22,694. [9] Poulet, F., et al. (2005) *Nature, 438*, 623-627. [10] Mustard, J. F., et al. (2008) *Nature, 454*, 305. [11] Carter, J., et al. (2010) *Science, 328*, 1682-1686. [12] Ehlmann, B. L., et al. (2011) *Clays and Clay Min., 59, 4*, 359-377. [13] Mustard, J. F., et al. (2011) *AGU Fall Meeting, P33H-05*. [14] Sinton W.M. (1967) *Icarus,6*, 222-228. [15] Milliken, R. E. and Mustard, J. F. (2005) *JGR Planets, 110, E12001*, doi: 10.1029/2005 JE002534. [16] Milliken, R. E. and Mustard, J. F. (2007a) *Icarus, 189, 2*, 574-588. [17] Milliken, R. E., et al. (2007b) *JGR Planets, 112, E08S07*, doi: 10.1029/2006 JE002853. [18] Jouglet, D., et al. (2007) *JGR Planets, 112, E08S06*, doi:10.1029/2006JE002846. [19] Leshin, L. A. and Vicenzi, E. (2006) *Elements, 2*, 157-162. [20] Gendrin, A., et al. (2005) *Science, 307*, 1587-1591. [21] Squyres, S. W., et al. (2004) *Science, 306*, 1709-1714. [22] Milliken, R. E., et al. (2008) *Geology, 36, 11*, 847-850. [23] Osterloo, M. M., et al. (2008) *Science, 319, 5870*, 1651-1654. [24] Christensen, P. R., et al. (2000) *JGR, 105, E4*, 9623-9642. [25] Bibring, J. -P., et al. (2007) *Science, 317, 5842*, 1206-1210. [26] Bibring, J. –P., et al. (2006) *Science, 312, 5772*, 400-404. [27] Mangold, N., et al. (2010) *Icarus, 207, 1*, 265-276. [28] Skok, J. R., et al. (2010) *Nature Geo.,* doi:10.1038/ngeo990. [29] Mangold, N., et al. (2007) *JGR Planets, 112, E08S04*, doi:10.1029/2006 JE002835. [30] Ehlmann, B. L., et al. (2009) *JGR Planets, 114, E00D08*, doi:10.1029/2009 JE003339. [31] Roach, L. H., et al. (2010) *Icarus, 206, 1*, 253-268. [32] Murchie, S. L., et al. (2009) *JGR, 114, E00D06*, doi: 10.1029/2009JE003342. [33] Flahaut, J., et al. (2011) *Icarus, in press*. [34] Fraeman, A. A., et al. (2009) *LPS XL*, #2320. [35] Poulet, F., et al. (2008) *Astron. Astrophys., 487, L41–L44*, doi:10.1051/0004-6361:200810150. [36] Carlson, R. L. (2003) *GRL, 30, 22*, 2142-2145. [37] Andrews-Hanna, J. C. and Lewis, K. W. (2011) *JGR, 116, E02007*, doi: 10.1029/2010JE003709.