Contributions from Hydrated States of $MgSO_4$ to the Reservoir of Hydrogen at Equatorial Latitudes on Mars.

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Introduction: Significant deposits of hydrogen have been observed within large areas near the equator of Mars [1]. The molecular associations of this hydrogen are not known. Several possibilities have been suggested: 1) buried water ice, 2) water molecules adsorbed on the surfaces of soil grains, 3) structural OH and interlayer H_2O in clays, 4) water associated with extra-framework cations in zeolites, and 5) structural OH and H_2O in salt hydrates.

In order to help sort through these possibilities we examine the stability of the various hydration states of $MgSO_4$ because the typical mass percent of anhydrous $MGSO_4$ is estimated to be about 10% [2], and $MgSO_4$ has three stable hydration states; kieserite ($MgSO_4.1H_2O$), hexahydrite ($MgSO_4.6H_2O$) and epsomite ($MgSO_4.7H_2O$). Where these minerals are stable, the water mass fraction they contain would be about 1.5% for kieserite, 8.3% for hexahydrite, and 9.5% for epsomite, comparable to the abundances of hydrogen observed near the equator of Mars [1].

Index of Stability: We develop maps of an index of stability given by the ratio of mean-annual water vapor density near the Martian surface to that density in equilibrium with surface soils at the mean annual temperature [3]. Where this index is greater than unity, water ice and/or hydrated states of Mg-sulfates are in equilibrium with the relative humidity of the atmosphere. Where this index is less than unity, their water will be lost to the atmosphere.

Map of Water-Equivalent Hydrogen: We start first with an overview of lower-limit estimates of the distribution of water-equivalent hydrogen (WEH) within the upper-most meter of Mars. Maps derived from a composite data set of CO_2 frost-free conditions measured using the Mars Odyssey Neutron Spectrometer, are shown in the top panel of Fig. 1 [1]. The contours drawn in this panel correspond to WEH mass percentages of 3%, 5.5%, and 8%. Inspection shows that relative enhancements in WEH maximize in Arabia Terra and Medusae Fossae at close to 10% by mass. This last maximum is connected to an azimuthally-extended reservoir that follows the zero-km elevation contour before connecting to the north-polar reservoir along the western margin of Tharsis, and through Elysium Mons [1]. Relative minima amounting to about 2% WEH by mass occur in isolated patches that overlap Syria Planum, Argyre basin, Hellas basin, Isidis Planitia, Utopia Planitia, northern Acidalia, Kassei Vallis, Chryse Planitia, and Elysium Planitia.

Stability Boundaries: There is a current dearth of information regarding the stability of hydrated minerals at temperatures and water-vapor densities that are relevant to the near equatorial zone of Mars. Best known is the relation between the frost-point vapor pressure, P [Pa], and temperature, T [K] for water ice, given by the Clausius-Clapeyron relation:

$$P\,[\mathrm{Pa}] = P_o \exp[-\Delta H/RT]. \qquad (1)$$

Here $P_o(\mathrm{Ice}) = 3.47 \times 10^{12}$ Pa, $\Delta H(\mathrm{Ice\text{-}Vapor}) = 50.87$ kJ/mol [4], and R=8.317 J/mol/K, the gas constant.

Similar stability boundaries in the form of Eq. 1 for the various hydrated states of $MgSO_4$ can be developed from recent laboratory work [5,6], although significant extrapolation to Martian conditions is necessary.

However, according to the work of Chou and Seal [5], hexahydrite may be metastable at temperatures below 284 K, and the only equilibrium relation below this point should be between epsomite and kieserite. On the other hand, preliminary work done by Vaniman et al. [6] shows that hexahydrite may be the dominant hydration state at Martian conditions even though it may only be metastable. We have therefore generated maps of stability indices for both the epsomite-kieserite boundary ($P_o(\mathrm{eps\text{-}kies}) = 4.38 \times 10^{12}$ Pa, $\Delta H(\mathrm{eps\text{-}kies}) = 54.05$ kJ/mol), and the epsomite-hexahydrite boundary ($P_o(\mathrm{eps\text{-}hex}) = 4.85 \times 10^{13}$ Pa, $\Delta H(\mathrm{eps\text{-}hex}) = 59.72$ kJ/mol) using Eq. 1 and [5]. The stability-index maps for water ice, the epsomite-kieserite boundary, and the epsomite-hexahydrite boundary, are shown in the bottom three panels of Fig. 1.

Starting first with the second panel from the top in Fig. 1, we note that water ice is unstable to evaporation everywhere within about 45^o of the equator (the boundary is shown in the panel by the jagged pink line threading the light purple color near $\pm 45^o$ latitude). Comparison of the 3%, 5.5%, and 8% WEH contours from the top panel, superimposed on the water-ice stability map in the next panel, shows a complete lack of correlation. Water ice is therefore an unlikely candidate for contributing to the equatorial reservoir of hydrogen sampled by neutrons on Mars.

Comparison of the same contours that overlay the epsomite-kieserite stability map in the second lowest panel shows a better correlation. There are regions where epsomite is stable relative to kieserite where WEH is high (e.g., the northern portions of Arabia Terra and of the east-west lane of high WEH centered at 10^o S and 180^o E). However, there are also many regions where WEH is relatively high and epsomite is unstable, such as just south of Arabia Terra and of the east-west lane of enhanced WEH centered at (10^o S, $+180^o$ E). In addition there are other regions (such as the southern portions of Argyre and Hellas, and of Amazonis Planitia) where epsomite is stable relative to kieserite yet WEH is relatively low. A similar comparison between contours of WEH abundances and the epsomite-hexahydrite stability map (given in the bottom panel of Fig. 1) shows no net improvement in overall correlation. Whereas better agreement is obtained in regions where WEH is high and epsomite is stable relative to hexahydrite, poorer agreement is obtained where WEH is low yet epsomite is stable.

Summary and Conclusions: A comparison of the domains of stability of water ice and three of the hydration states of $MgSO_4$ with lower-limit measurements of the abundance of WEH at equatorial latitudes on Mars, shows that water ice is unlikely to be responsible for the reservoirs of WEH measured using the Mars Odyssey Neutron Spectrometer. In addition, our analysis shows that both epsomite and hexahydrite could contribute significantly over large areas near the equator where $MgSO_4$ is present. Where $MgSO_4$ is present but epsomite and hexahydrite are not stable, kieserite is stable and may therefore contribute to the WEH inventory. This last possibility is supported by the fact that the contribution of kieserite to WEH (1.5%) when added to the contribution of adsorbed water (~0.5% [5]) on regolith grains, can account entirely for the minimum abundance of WEH observed at equatorial latitudes (2% [1]).

However, the overall poor correlation between the stability boundaries of epsomite and hexahydrite with measured WEH abundances seen in Fig. 1 shows that other factors must also contribute. For example, hydrated states of other minerals such as clays and zeolites may contribute importantly to the WEH inventory on Mars [6,7]. Additionally, the abundance of $MgSO_4$ may vary considerably geographically over the surface near the equator. It is also possible that most of the $MgSO_4$ present is amorphous, with a poorly defined hydration state between epsomite and kieserite [8]. A last possibility is that the mean annual subsurface vapor densities and temperatures estimated from assumptions of the structure of near surface soils (parameterized by their albedo and thermal inertia [3]) may not be applicable over the depths that contain the observed reservoir of WEH at all geographic locations.

References: [1] Feldman, W.C., et al., JGR, accepted, 2003. [2] Wänke, H., et al., Spa, Sci. Rev., 96, 317-330, 2001. [3] Mellon, M.T. et al., ICARUS, in press, 2003. [4] Möholmann, D.T.F., ICARUS, in press, 2003. [5] Chou, I.M., and R.R. Seal, Astrobiology, in press, 2003. [6] Vaniman, D.T., et al., LPS XXXV, 2004, [7] Basilevsky, A.T, et al., Solar System Research, 37, 387-396, 2003. [8] Bish, D.L. et al., 6th Int. Mars Conf., 2003.

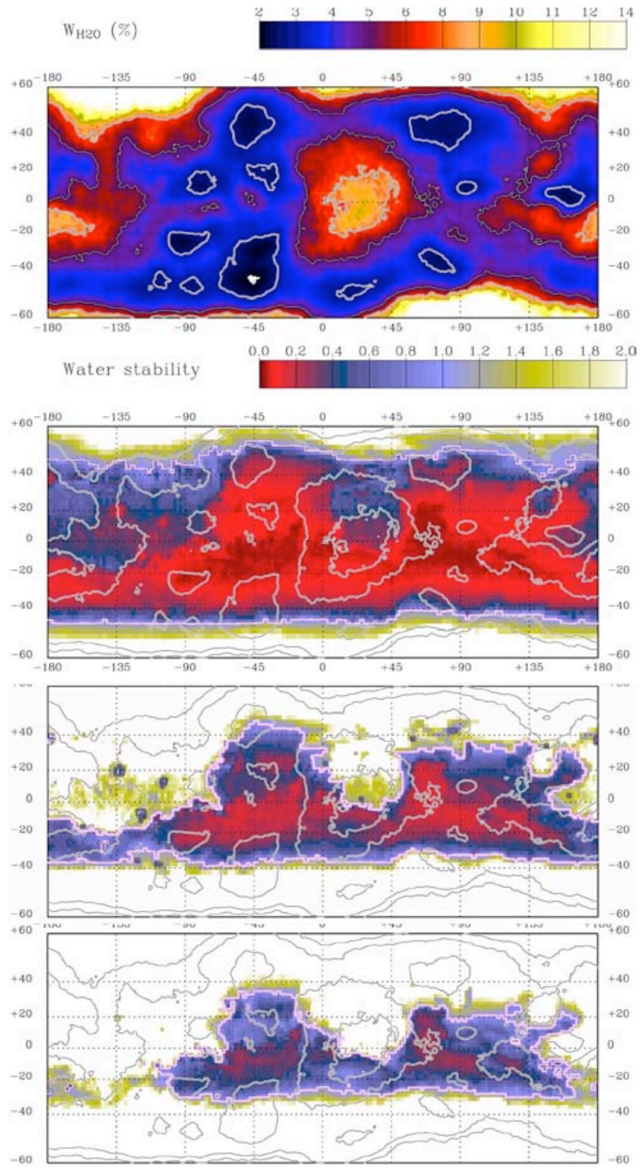

Figure 1: From top to bottom, are maps of WEH, and the stability indices of water ice-vapor, epsomite-kieserite, and epsomite-hexahydrite. The contours in the WEH map correspond to 3% (enclosing the black color), 5.5% and 8% (enclosing the orange color) WEH by mass. These contours are included as white lines in the other three panels. The stability boundaries in these lower three panels are given by the 1.0 contour drawn between the light blue and yellow colors as a thick jagged pink line.