CAN HYDROUS MINERALS ACCOUNT FOR THE OBSERVED MID-LATITUDE WATER ON MARS?

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Introduction: Great interest was generated with the discovery by the Odyssey spacecraft of heterogeneously distributed hydrogen at martian mid-latitudes, suggesting that large areas of the near-equatorial highlands contain near-surface deposits of "chemically and/or physically bound H_2O and/or OH" in amounts up to 3.8% equivalent H_2O [1]. More recent interpretations of the Odyssey data using new calibrations suggest that some near-equatorial areas, such as Arabia Terra, contain up to 8.5±1.3% water-equivalent hydrogen [2]. Such shallow occurrences (<1 m) of H_2O ice near the martian equator are particularly enigmatic because H_2O ice is not stable at these latitudes [3, 4]. A number of potentially hydrous silicate phases, notably clay minerals and zeolites, have been proposed as possible H_2O-bearing constituents on Mars, and both groups of minerals are common terrestrial alteration products of hydrovolcanic basaltic ashes and palagonitic material comparable to those that may be widespread on Mars [*e.g.*, 5]. Smectites within martian meteorites, attributed to hydrous alteration on Mars rather than on Earth [6], provide direct evidence of clay minerals from Mars. In addition, new thermal emission spectrometer (TES) data provide evidence for unspecified zeolites in martian surface dust [7], and [8] concluded that spectral deconvolution of MGS TES and Mariner 9 IRIS data is consistent with the presence of zeolite in the martian surface dust.

In addition to these hydrous silicates, Mg-sulfates are indicated in XRF analyses of Viking regolith samples and in APXS analyses of Pathfinder soils and rocks, where S, Cl, and possibly Mg are implicated as products of rock alteration and soil "duricrust" development [9]. Salts of these elements may be highly hydrated, but the stabilities of hydrated sulfates (or chlorides) at martian surface conditions are poorly known. Other hydrated salts (*e.g.*, nitrates, carbonates) may be present but are as-yet undetected by the instruments deployed. There is a large variety of H_2O-rich sulfate and chloride minerals; among these both simple Mg-sulfate salts (*e.g.*, epsomite, $Mg(H_2O)_6(SO_4)(H_2O)$) and more complex Mg-bearing sulfates (*e.g.*, blödite, $Na_2(Mg(H_2O)_4(SO_4)_2)$) have been proposed as possible cementing agents in martian regolith [9].

Clays, zeolites, and Mg-sulfates are all phases that could potentially retain H_2O in martian regolith. The nature of the hydrogen-containing material observed in the equatorial martian regolith is of particular impor-

tance to the question of whether hydrous minerals have formed in the past on Mars. Also, whether these minerals exist in a hydrated (*i.e.*, containing H_2O molecules in their structures) or dehydrated state is a crucial question. The purpose of this communication is to estimate the possible magnitude of the H_2O reservoir constituted by these H_2O-bearing minerals. In other words, can minerals containing H_2O and/or OH such as clays, zeolites, or Mg-sulfates, reasonably be expected to account for the amounts of near-equatorial H_2O-equivalent hydrogen recently documented by Mars Odyssey?

Hydrous and Hydrate Minerals: Hydrous minerals, including zeolites and clays, are phases in which H_2O may be present in highly variable amounts depending on environmental conditions, without changing the crystal structure. Phyllosilicate clay minerals, along with a variety of other minerals such as amphiboles, also contain smaller amounts of hydroxyl groups in their structures. Hydrate minerals are those in which H_2O occurs in relatively fixed amounts, and loss or gain of H_2O is, in general, accompanied by formation of a different crystal structure (*e.g.*, gypsum, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$). Clinoptilolite $[(Na,K,1/2Ca)_6Al_6Si_{30}O_{72} \cdot \sim 20H_2O]$, the most common terrestrial natural zeolite, is a hydrous tectosilicate containing large structural channels formed by ten-membered and eight-membered rings. Substitution of Al^{+3} for Si^{+4} in the framework gives rise to a net negative charge on the framework, balanced by exchangeable cations in the extraframework sites. The extraframework sites in these channels contain exchangeable Na, K, and/or Ca, along with H_2O. Similarly, the chabazite $(Ca_2Al_4Si_8O_{24} \cdot \sim 12H_2O)$ structure is made up of four- and eight-membered rings, and the large elliptical extraframework sites contain both exchangeable Ca and H_2O molecules.

Smectites are hydrous phyllosilicate clay minerals with a layer structure based on two opposed sheets of corner-linked Al-Si tetrahedra sandwiching a sheet of edge-linked octahedra. Similar to the zeolites, substitutions in both tetrahedral and octahedral sheets give rise to a net negative charge on the individual layers, balanced by exchangeable cations in the regions between the tetrahedral-octahedral-tetrahedral "sandwiches" (*i.e.*, the interlayer region). In addition to exchangeable cations (typically Na, K, and Ca, but also Mg), the interlayer contains a variable amount of H_2O mole-

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cules, in addition to a fixed amount of OH within the sheets.

The list of conceivable hydrated salts in the martian regolith is daunting and includes a variety of Mg sulfates and chlorides, in addition to possible hydrous carbonates or others. There are at least 16 different hydrated Mg-bearing sulfates that can contain over 20 wt% H_2O; this does not include the many hydrous chlorides and carbonates that may also contain Mg. We have begun by examining the simplest and most commonly cited series relevant to Mars, the basic $MgSO_4$ hydrates. Hydrated salts such as Mg-sulfates exist with a variety of crystal structures, with H_2O molecules present both as integral parts of the structures and as guest molecules. H_2O can be reversibly removed from the latter structures (*e.g.*, epsomite dehydrating to hexahydrite) without large structural changes. In contrast, removal of H_2O from hexahydrite [$Mg(H_2O)_6(SO_4)$] causes destruction of the structure, as H_2O molecules directly coordinate the Mg cations.

Hydration/dehydration energetics: It is possible to obtain quantitative information on the energetics of the hydration/dehydration process in hydrous minerals using quantitative thermoanalytical data. For example, [10] quantified the thermodynamics of hydration in clinoptilolite by measuring isothermal gravimetric data under conditions of controlled $P(H_2O)$. From these thermodynamic data, it is possible to model the hydration state of hydrous minerals under assumed martian surface temperatures and partial pressures of H_2O.

Based on analysis of thermoanalytical data, [11, 12, 13] showed that the H_2O-bearing minerals smectite, clinoptilolite, and chabazite may exist in partially hydrated states on the surface of Mars, in spite of the low partial pressure of H_2O. That is, these minerals may contain H_2O in their interlayers (smectites) or in their extraframework sites (zeolites) under present-day martian equatorial surface conditions. These simulations are based on equilibrium thermodynamic data, and the conclusions are not affected by kinetic factors.

Methods and Results (Smectites): Using isothermal gravimetric methods, together with published data on the partial molar enthalpies of smectite hydration at 25°C [14], [12] formulated a thermodynamic description that can be used to simulate the hydration state of Na- and Ca-smectite under martian surface conditions. Measured data on the chemical potential of sorbed H_2O in smectite (isothermal gravimetric experiments done under controlled $P(H_2O)$) were combined with enthalpy values derived from [14] to obtain the chemical potential of H_2O in smectite at a given T and $P(H_2O)$, *i.e.*, under estimated martian surface conditions. The results of this simulation are in Figure 1.

Unlike zeolites, which have maximum H_2O contents constrained by the volume of the extraframework sites, the layer structure of smectites provides much less constraint. Smectite hydration occurs initially in a stepwise fashion, with approximately integral numbers of H_2O layers occurring between the silicate sheets. Because the layer structure is not three-dimensionally connected, the layers can expand as increasing amounts of H_2O occupy the interlayer region. This stepwise hydration behavior can be seen in Figure 1. Na-smectite contains <5% H_2O at the martian subsurface temperature. On the other hand, Ca-smectite retains a higher fraction of its water content, up to ~10 wt.% H_2O at 215K.
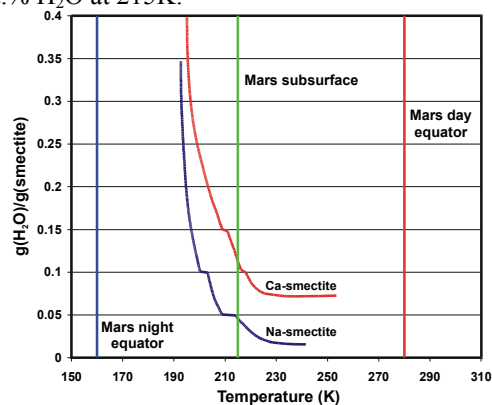

Figure 1. Hydration state of Na- and Ca-smectites as a function of T at a $P(H_2O)$ of 1.5 x 10^{-6} bars. Approximate Mars subsurface T and night and day T's at the equator are shown. Note stepwise behavior of both smectites at low H_2O contents

Methods and Results (Clinoptilolite): Equilibrium isothermal gravimetric measurements on cation-exchanged samples of clinoptilolite gave a thermodynamic formulation for the sorption of H_2O in Na-, K-, and Ca-clinoptilolite [10]. Gravimetric data were measured from 25 to 250°C and from 0.2 to 35 mbar H_2O vapor pressure using a thermogravimetric analyzer with automated relative humidity (RH) control.

By solving eq. 12 in [10] for the value of θ as a function of T at a $P(H_2O)$ =1.5 x 10^{-6} bars, the hydration state of these three cation-exchanged forms of clinoptilolite under expected martian surface conditions was simulated [12]. Results are shown in Figure 2, expressed as the parameter θ, or fractional H_2O occupancy, vs. T. Combining these simulations with the maximum H_2O contents of Na-, K-, and Ca-clinoptilolite, 15.7, 13.5, and 16.3% H_2O, respectively [10], provides an estimate of the approximate weight fractions of H_2O in clinoptilolite on the martian surface. The data in Fig. 2 show that all three cation-exchanged forms of clinoptilolite would have ~90% of

CAN HYDROUS MINERALS ACCOUNT FOR THE OBSERVED MID-LATITUDE WATER ON MARS?: D. L. Bish *et al.*

their maximum H_2O contents noted above (14.1, 12.2, and 14.7 wt.% H_2O for the Na-, K-, and Ca- forms, respectively) at or below the martian subsurface temperature (for a $P(H_2O)$ of 1.5 x 10^{-6} bars).

However, Fig. 2 also suggests that, if exposed to equatorial day temperatures, all three forms of clinoptilolite would dehydrate significantly, Na-clinoptilolite to ~47%, the K form to ~36%, and the Ca form to ~52% hydrated. For pure clinoptilolite samples, these values equate to 7.4, 4.9, and 8.5 wt. %, respectively.
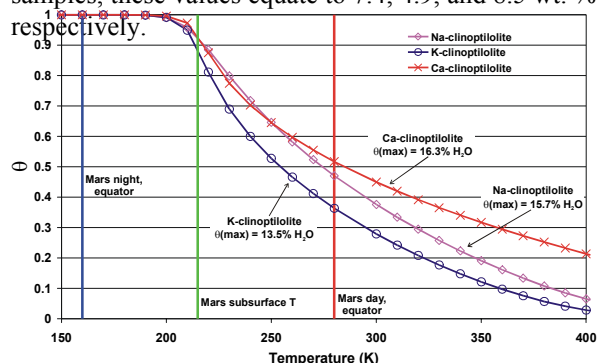

Figure 2. Hydration state of Na-, K-, and Ca-clinoptilolites as a function of T at a $P(H_2O)$ of 1.5 x 10^{-6} bars. Approximate Mars subsurface T and Mars night and day T's at the equator are shown.

Methods and Results (Chabazite): The thermodynamics of hydration/dehydration of chabazite were recently analyzed using a combination of dynamic (thermogravimetric analysis, TGA) and isothermal measurements on natural chabazite [13, 15]. Thermal data were measured using a DuPont 951 thermogravimetric analyzer with automated RH control. Unlike clinoptilolite, whose gravimetric data could be fit assuming a single type of H_2O, both dynamic TGA data and isothermal data support the existence of three energetically distinct types of H_2O in chabazite. Initial attempts to fit all isotherms using the methods of [10] provided poor fits and unrealistic thermodynamic data. Therefore, the dynamic and isothermal data were analyzed using three independent sets of thermodynamic parameters. H_2O site 1, occupied only under low-T and/or high $P(H_2O)$ conditions, contains up to 8.4 wt.% H_2O. Site 2 contains up to 10.8 wt.% H_2O, and site 3 contains up to 3.2 wt.% H_2O. Site 3 is occupied in all but the highest-T and low-$P(H_2O)$ conditions. These three sites combine for a total of 22.4 wt.% H_2O in fully hydrated chabazite.

By solving eq. 12 in [10] for the value of θ as a function of T at a fixed $P(H_2O)$ (1.5 x 10^{-6} bars), [13] simulated the hydration state of chabazite under expected martian surface conditions. The results of these simulations are shown in Figure 3, expressed as the

parameter θ, or fractional H_2O occupancy, for site-1 and site-2 H_2O vs. T. H_2O site 3 is of such high enthalpy that it is fully hydrated under all possible martian surface conditions and is not shown on Figure 3.
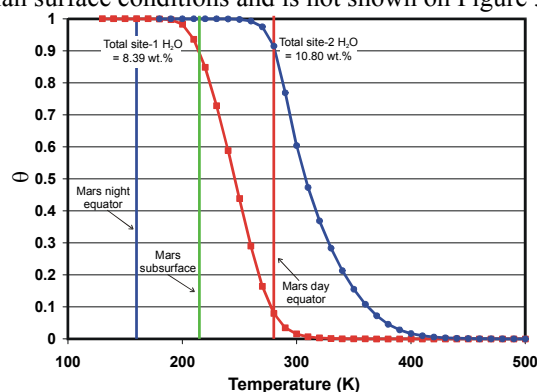

Figure 3. Fractional H_2O content of chabazite, calculated for a $P(H_2O)$ of 1.5 x 10^{-6} bars for both H_2O site 1 and 2 (from isothermal TGA data).

This figure shows that H_2O site 2 would be virtually full under most plausible martian surface conditions, although higher T or lower $P(H_2O)$ values would begin to dehydrate this site. This figure suggests that H_2O site 1 would vary from fully occupied to almost empty over a daily temperature cycle at the equator, and this site would be largely occupied at subsurface temperatures. Chabazite similar to the sample we studied would contain slightly less than its maximum 22.4 wt.% H_2O under martian subsurface temperatures, assuming the $P(H_2O)$ used in these simulations, with site 1 ~90% full and sites 2 and 3 full (giving a total H_2O content of 21.6 wt.% at subsurface T's).

Methods and Results (Mg-sulfates): Thermal analyses of Mg-sulfates similar to those discussed above for zeolites and smectites are limited, and, to our knowledge, a complete thermodynamic description of the hydration/dehydration process in any of the basic hydrated Mg-sulfates is not available. Thus, it is not presently possible to determine the theoretical stability limits for the variety of hydrates suggested to occur on the martian surface. In a study on the stability of hydrated salts on the surface of Europa, [16] used temperature-programmed desorption (TPD) measurements of epsomite to determine whether this sulfate might remain hydrated under Europa surface conditions (<130 K). Their kinetic data (their Fig. 5) suggest that epsomite would not remain hydrated under martian equatorial surface conditions for more than ~10 years. We have just begun experiments with hydrated Mg-sulfates, and preliminary results with epsomite and hexahydrite indicate extreme sensitivity of crystal structure to environmental conditions. We experimentally analyzed the dehydration behavior of epsomite

CAN HYDROUS MINERALS ACCOUNT FOR THE OBSERVED MID-LATITUDE WATER ON MARS?: D. L. Bish *et al.*

and the isostructural mineral hexahydrite, $Mg(H_2O)_6(SO_4)$, from 100 to 295K and from 20 mtorr total pressure to room conditions (~1 torr and <10% RH). We also measured the response of epsomite at 295K to changes in RH from 0 to ~70%. Our results show that epsomite is not stable at 295K at RH values less than about 55%, below which hexahydrite is the observed phase. More importantly for applications to Mars (and Europa), our experiments demonstrate that hexahydrite is not stable at pressures down to ~20 mtorr. Figure 4 shows the X-ray powder diffraction patterns of a specimen of hexahydrite held at 273K and ~20 mtorr for six h. Diffraction pattern #1, taken in room air (~7%RH) at 273K represents the pattern for hexahydrite; subsequent patterns (2-5) measured at ~20 mtorr reflect the increasing breakdown of hexahydrite to an amorphous hydrated $MgSO_4$ (#6). Amorphization was not apparent in 2 h at 100K but became obvious on a 1-h time scale at 273 K. Thermogravimetric analysis of this amorphous solid shows that it contains ~26 wt.% H_2O, and its observed macroscopic expansion behavior suggests that this amorphous solid can reversibly hydrate and dehydrate.
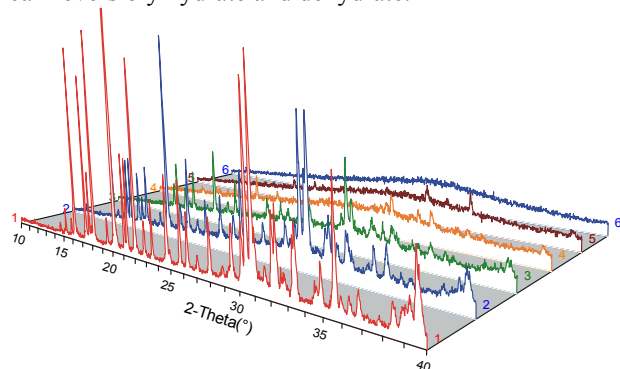

Figure 4. Time-resolved XRD patterns of hexahydrite, 273K, 20 mtorr, taken at ~1 hr intervals.

Given the description of the TPD studies on epsomite in [16] (samples were handled at ~4°C and chamber evacuation to 10^{-9} torr began at ~0°C), it appears likely that their kinetic data reflect the behavior of an amorphous hydrated $MgSO_4$ rather than epsomite (or hexahydrite). More importantly, our preliminary data on epsomite and hexahydrite illustrate that neither of these phases is a reasonable candidate for a hydrated $MgSO_4$ on the surface of Mars. If hydrated $MgSO_4$ is present on the surface of Mars, one of the crystalline lower hydrates or amorphous $MgSO_4 \cdot nH_2O$ is a more-likely candidate; considerable further research is required on these phases.

Summary and Conclusions: Quantitative analysis of the thermal data for smectite, clinoptilolite, chabazite, and hydrated $MgSO_4$ give bounds on the amount of each of these phases that would be required to account for the amounts of H_2O documented by [2]. The average H_2O content of most equatorial regions, ~4% [2], can be accounted for by ~40% Ca-smectite or 20% chabazite, without calling on any hydration in the duricrust salts recognized in such terrains by the Viking landers. However, large amounts of these phases (40%-85%), or lesser amounts of a hydrous salt such as alunogen $(Al_2(SO_4) \cdot 17H_2O)$ [17], which contains ~47% water if fully hydrated, would be required in the upper 1 m to account for the value of ~8.5 wt.% H_2O in Arabia Terra. Locally large areas (10's of km) of Earth's surface contain elevated zeolite and hydrated sulfate contents (*e.g.*, saline, alkaline-lake deposits associated with volcanic ash deposits and closed basins, such as deposits associated with the Messinian Salinity Crisis), and smectites are ubiquitous soil phases. However, in spite of the common terrestrial occurrence of many of the phases discussed here, unusually large quantities of these phases are required to account for the amounts of water found by [2]. Considerably more data are required to determine with certainty whether the elevated H_2O contents of the upper 1 m found by Odyssey can be ascribed to mineralogical phenomena rather than to unusual hydrologic conditions. Nevertheless, there appears to be sufficient chemical and hydration thermodynamic evidence to indicate that hydrous and hydrate minerals have the potential to play a role in the near-surface martian water budget.

References: [1] Feldman W.C. et al. (2002) *Science, 297*, 75-78. [2] Feldman W.C. et al. (2003) *this volume.* [3] Paige, D.A. (1992) *Nature, 356*, 43-45. [4] Mellon M.T. and Jakosky B.M. (1993) *J. Geophys. Res.-Planets, 98*, 3345-3364. [5] Golden D.C. et al. (1993) *J. Geophys. Res.-Planets, 98*, 3401-3411. [6] Treiman A.H. et al. (1993) *Meteoritics, 28*, 86-97. [7] Ruff S.R. (2002) *EOS (Spring Suppl.), 83*, P31A-08. [8] McSween H.Y., Jr. et al. (2003) *LPSC XXXIV*, CD #1233. [9] Clark B.C. and VanHart D.C. (1981) *Icarus, 45*, 370-378. [10] Carey J.W. and Bish D.L. (1996) *Amer. Mineral., 81*, 952-962. [11] Bish D.L. et al. (2002) *LPSC XXXIII*, CD #1895. [12] Bish D.L. et al. (2003) *Icarus*, in press. [13] Bish D.L. et al. (2003) *LPSC XXXIV*, CD #1786. [14] Dios Cancela G. et al. (1997) *J. Coll. Int. Sci., 185*, 343-354. [15] Fialips C.I. et al. (2003) *Euroclay proceedings*. [16] McCord et al. (2001) *J. Geophys. Res., 106*, 3311-3319. [17] Banin A. et al. (1997) *J. Geophys. Res., 102*, 12341-13356.