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 H₂O and/or OH" in amounts up to 3.8% equivalent H₂O [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 H₂O ice near the martian equator are particularly enigmatic because H₂O 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 H₂O-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 H₂O-rich sulfate and chloride minerals; among these both simple Mg-sulfate salts (e.g., epsomite, Mg(H₂O)₆(SO₄)(H₂O)) and more complex Mg-bearing sulfates (e.g., blödite, Na₂(Me(H₂O)₆(SO₄)₂) have been proposed as possible cementing agents in martian regolith [9].

Clays, zeolites, and Mg-sulfates are all phases that could potentially retain H₂O in martian regolith. The nature of the hydrogen-containing material observed in the equatorial martian regolith is of particular importance 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 H₂O molecules in their structures) or dehydrated state is a crucial question. The purpose of this communication is to estimate the possible magnitude of the H₂O reservoir constituted by these H₂O-bearing minerals. In other words, can minerals containing H₂O and/or OH such as clays, zeolites, or Mg-sulfates, reasonably be expected to account for the amounts of near-equatorial H₂O-equivalent hydrogen recently documented by Mars Odyssey?

Hydrous and Hydrate Minerals: Hydrous minerals, including zeolites and clays, are phases in which H₂O 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 H₂O occurs in relatively fixed amounts, and loss or gain of H₂O is, in general, accompanied by formation of a different crystal structure (e.g., gypsum, CaSO₄·2H₂O, and anhydrite, CaSO₄). Clinoptilolite [(Na,K,1/2Ca)₂Al₄Si₄O₁₂·2H₂O], the most common terrestrial natural zeolite, is a hydrous tectosilicate containing large structural channels formed by ten-membered and eight-membered rings. Substitution of Al³⁺ for Si⁴⁺ 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 H₂O. Similarly, the chabazite (Ca₂Al₄Si₄O₁₂·12H₂O) structure is made up of four- and eight-membered rings, and the large elliptical extraframework sites contain both exchangeable Ca and H₂O 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 in-
terlayer contains a variable amount of H$_2$O molecules, 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$_2$O; 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$_2$O molecules present both as integral parts of the structures and as guest molecules. H$_2$O can be reversibly removed from the latter structures (e.g., epsomite dehydrating to hexahydrite) without large structural changes. In contrast, removal of H$_2$O from hexahydrite [Mg(H$_2$O)$_6$(SO$_4$)] causes destruction of the structure, as H$_2$O 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$_2$O). 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$_2$O.

Based on analysis of thermoanalytical data, [11, 12, 13] showed that the H$_2$O-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$_2$O. That is, these minerals may contain H$_2$O 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$_2$O in smectite (isothermal gravimetric experiments done under controlled P(H$_2$O)) were combined with enthalpy values derived from [14] to obtain the chemical potential of H$_2$O in smectite at a given T and P(H$_2$O), i.e., under estimated martian surface conditions. The results of this simulation are in Figure 1. Unlike zeolites, which have maximum H$_2$O 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$_2$O layers occurring between the silicate sheets. Because the layer structure is not three-dimensionally connected, the layers can expand as increasing amounts of H$_2$O occupy the interlayer region. This stepwise hydration behavior can be seen in Figure 1. Na-smectite contains <5% H$_2$O at the martian subsurface temperature. On the other hand, Ca-smectite retains a higher fraction of its water content, up to ~10 wt.% H$_2$O at 215K.

**Methods and Results (Clinoptilolite):** Equilibrium isothermal gravimetric measurements on cation-exchanged samples of a natural clinoptilolite sample gave a thermodynamic formulation for the sorption of H$_2$O in Na-, K-, and Ca-clinoptilolite [10]. Gravimetric data were measured from 25 to 250°C and from 0.2 to 35 mbar H$_2$O vapor pressure using a DuPont 951 thermogravimetric analyzer with automated relative humidity (RH) control.

By solving eq. 12 in [10] for the value of $\theta$ as a function of T at a P(H$_2$O) = 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 $\theta$, or fractional H$_2$O occupancy, vs. T. Combining these simulations with the maximum H$_2$O contents of Na-, K-, and Ca-clinoptilolite, 15.7, 13.5, and 16.3% H$_2$O, respectively [10], provides an estimate of the approximate weight fractions of H$_2$O in clinoptilolite on the martian surface. The data in Fig. 2 show that all three cation-exchanged forms of clinoptilolite would have ~90% of...
their maximum H₂O contents noted above (14.1, 12.2, and 14.7 wt.% H₂O for the Na-, K-, and Ca- forms, respectively) at or below the martian subsurface temperature (for a P(H₂O) of 1.5 x 10⁶ 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.

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 H₂O, both dynamic TGA data and isothermal data support the existence of three energetically distinct types of H₂O 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. H₂O site 1, occupied only under low-T and/or high P(H₂O) conditions, contains up to 8.4 wt.% H₂O. Site 2 contains up to 10.8 wt.% H₂O, and site 3 contains up to 3.2 wt.% H₂O. Site 3 is occupied in all but the highest-T and low-P(H₂O) conditions. These three sites combine for a total of 22.4 wt.% H₂O in fully hydrated chabazite.

By solving eq. 12 in [10] for the value of θ as a function of T at a fixed P(H₂O) (1.5 x 10⁶ 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 H₂O occupancy, for site-1 and site-2 H₂O vs. T. H₂O 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.

This figure shows that H₂O site 2 would be virtually full under most plausible martian surface conditions, although higher T or lower P(H₂O) values would begin to dehydrate this site. This figure suggests that H₂O 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.% H₂O under martian subsurface temperatures, assuming the P(H₂O) used in these simulations, with site 1 ~90% full and sites 2 and 3 full (giving a total H₂O 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...
and the isostructural mineral hexahydrite, Mg(H₂O)₆(SO₄)₂, 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 hours. 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 MgSO₄ (#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.% H₂O, 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 MgSO₄ 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 MgSO₄ on the surface of Mars. If hydrated MgSO₄ is present on the surface of Mars, one of the crystalline lower hydrates or amorphous MgSO₄•nH₂O 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 MgSO₄ give bounds on the amount of each of these phases that would be required to account for the amounts of H₂O documented by [2]. The average H₂O 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 (Al₂(SO₄)·17H₂O) [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.% H₂O 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 these 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 H₂O 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 hydrated mineral minerals have the potential to play a role in the near-surface martian water budget.

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**References:**