

Investigation of the water sorption properties of Mars-relevant micro- and mesoporous minerals

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Abstract

Encouraged by recent results of the Mars Odyssey spacecraft mission and the OMEGA team (Mars Express) concerning water in equatorial latitudes between $\pm 45^\circ$ on Mars and the possible existence of hydrated minerals, we have investigated the water sorption properties of natural zeolites and clay minerals close to martian atmospheric surface conditions as well as the properties of Mg-sulfates and gypsum. To quantify the stability of hydrous minerals on the martian surface and their interaction with the martian atmosphere, the water adsorption and desorption properties of nontronite, montmorillonite, chabazite and clinoptilolite have been investigated using adsorption isotherms at low equilibrium water vapor pressures and temperatures, modeling of the adsorption equilibrium data, thermogravimetry (TG), differential scanning calorimetry (DSC), and proton magic angle spinning nuclear magnetic resonance measurements (^1H MAS NMR). Mg-sulfate hydrates were also analyzed using TG/DSC methods to compare with clay mineral and zeolites. Our data show that these microporous minerals can remain hydrated under present martian atmospheric conditions and hold up to 2.5–25 wt% of water in their void volumes at a partial water vapor pressure of 0.001 mbar in a temperature range of 333–193 K. Results of the ^1H MAS NMR measurements suggest that parts of the adsorbed water are liquid-like water and that the mobility of the adsorbed water might be of importance for adsorption-water-triggered chemistry and hypothetical exobiological activity on Mars.

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1. Introduction

Recently documented results of the NASA Mars Odyssey spacecraft (Feldman et al., 2004) using the gamma-ray spectrometer instrument suite (Boynton et al., 2004) show deposits on Mars containing 2–11% water-equivalent hydrogen by mass for equatorial latitudes between $\pm 45^\circ$. Present martian thermal conditions suggest that this (most likely) water molecules cannot be liquid bulk water or water ice, and Möhlmann (2004) concluded that it could consist at least partially of “adsorption water.” The possible presence of water-bearing minerals such as zeolites and smectites in a hydrated state under martian sur-

face conditions was evaluated by Zent and Quinn (1997) and Bish et al. (2003a, 2003b), Vaniman et al. (2004) and Fialips et al. (2005) discussed the stability of hydrated magnesium sulfates. Spectral evidence for the existence of zeolites in the dust of Mars was given by Ruff (2004).

The latest results of the OMEGA team (Bibring et al., 2005; Gendrin et al., 2005) support the existence of a number of hydrated phyllosilicates and sulfates on the martian surface. Using the visible-near-infrared hyperspectral reflectance imagery on board the ESA Mars Express mission, hydrated materials such as nontronite, gypsum, kieserite, polyhydrated magnesium sulfates, and many others could be identified.

In the present paper, we report the results of experimental studies of the water sorption properties of several of these minerals under close to martian surface conditions (temperature

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and humidity) in mid- and low-latitudes. To obtain additional information on the stability of sulfate hydrates under martian conditions, the energetics of dehydration of some of the Ca- and Mg-sulfate hydrates have been investigated to compare with natural zeolites and smectites. The goal of our research is to provide a better understanding of the unexpected high water concentrations in the martian regolith in equatorial regions observed by the Mars Odyssey spacecraft and the Mars Express mission and also to evaluate possible consequences of the site of this water.

2. Experimental and modeling

2.1. Materials and methods

The sorption (hydration/dehydration) properties of chabazite (Wassons Bluff, Nova Scotia), clinoptilolite (sample 27054, Fish Creek Mountains, Nevada, USA) Ca-montmorillonite (STx, Gonzales County, Texas, USA) and nontronite (Femontmorillonite, NG-1, Hoher Hagen, Darnsfeld, Göttingen, Germany) were investigated by means of isotherm measurements, thermogravimetry (TG), differential scanning calorimetry (DSC), microcalorimetric measurements and ^1H MAS NMR. The dehydration of synthetic sulfates, including gypsum and the mono-, hexa- and heptahydrate of Mg-sulfate were evaluated by TG and DSC.

Sorption isotherms were measured gravimetrically from 257–333 K with a McBain quartz spring balance (sensitivity 4 mg/mm) equipped with two MKS Baratron pressure sensors covering a range of 10^{-5} –10 mbar (see also Jänchen et al., 2004, 2005). Before each adsorption experiment about 150–200 mg of material was heated for 2–3 h at 573 K (zeolites) and 393 K (clays) in high vacuum ($<10^{-5}$ mbar) to remove the adsorbed water. Previous results (e.g., Bish et al., 2003a, 2003b) illustrate that these treatments do not remove all water molecules associated with the mineral crystal structures, but these temperatures were chosen to maximize water loss and minimize possible crystal structure destruction.

The TG/DSC measurements were performed on a SETARAM TG-DSC 111 apparatus with a heating rate of 3 K/min from ambient up to 673 K. Prior to the experiments the samples (ca. 12–14 mg of zeolite or clay) were hydrated at a relative water pressure of $p/p_s = 0.3$. The sulfates were used as synthesized.

Heat curves of the porous materials (differential molar heats of adsorption) were determined with a SETARAM Calvet-type C 80 microcalorimeter equipped with a volumetric adsorption apparatus (see also Jänchen et al., 2005, for more details).

^1H MAS NMR experiments (proton magic-angle spinning NMR) were carried out on a BRUKER AVANCE 400 spectrometer with a Larmor frequency of 400 MHz and a magnetic field of 9.4 T. In order to optimize resolution, a spinning rate (MAS frequency) 10 kHz was used. Samples were equilibrated under room temperature and humidity conditions before measurement.

2.2. Modeling

The characteristic curves of the adsorption systems and other relevant dependences such as isotherms, isobars, and isosteres can be calculated using the Dubinin theory of pore filling (Dubinin, 1960). The Dubinin approach considers the pore volume as crucial (in contrast to the inner surface of the micropores) because the adsorbed molecules (comparable in size with the micropores) are influenced by overlapping adsorption potentials generating large heats of adsorption. Dubinin defines the specific volume, W , of the adsorption space (cavities and pores in cm^3 of the microporous material in g) as:

$$W = a/\rho_{\text{ads}}, \quad (1)$$

where a = adsorbed amount (g/g), depending on T and p , and ρ_{ads} = density of the adsorbate (g/cm^3), depending on T , and the differential work of adsorption, A , is defined as:

$$A = -\Delta f = RT(\ln p_s/p), \quad (2)$$

where Δf = free energy and p_s = vapor pressure of the adsorptive in equilibrium with the liquid bulk phase at the analysis temperature, Dubinin (1960) found for many adsorption systems with activated carbon that almost all experimental systems have a single curve relating W and A . The relation $W = f(A)$ is called the “characteristic curve” that is temperature invariant for many adsorption systems (for further details see Stach et al., 2005). The results of our isotherm measurements were extrapolated to 193 K using this approach to obtain isobars from the measured data between 0.0001 and 0.1 mbar of partial water pressure covering the expected rather low average water vapor pressure values of 0.001 mbar and low temperatures on the martian surface.

3. Results and discussion

Water adsorption and desorption isotherms for chabazite and clinoptilolite from 257–333 K and over seven orders of magnitude (10^{-5} –10 mbar) in partial pressure of water are shown in Figs. 1 and 2. The isotherms were typically S-shaped, with some indication of steps probably related to the presence of H_2O molecules in different locations in the zeolite framework (Bish et al., 2003a, 2003b; Carey and Bish, 1996). The maximum water adsorbed for chabazite amounts to ~ 25 wt% and that of clinoptilolite to ~ 15 wt%. The water content of the materials under martian conditions typically will differ from these maximum values due to changes in pressure and temperature.

As seen in Fig. 1, chabazite accommodated up to 0.2 g/g (corresponds to 20 wt%) water at 257 K and ~ 0.001 mbar (see dashed line in the figure, indicating the approximate partial pressure of water on the martian surface). Increasing temperature had the effect of lowering the water content of chabazite, but even at 333 K about 0.05 g/g (5 wt%) water was retained by this zeolite. Clinoptilolite (Fig. 2) adsorbed about 0.08 g/g at the same pressure and 257 K, and a small amount of water remained (0.025 g/g, 2.5 wt%) even when the temperature was increased to 333 K. Neither clinoptilolite nor chabazite showed

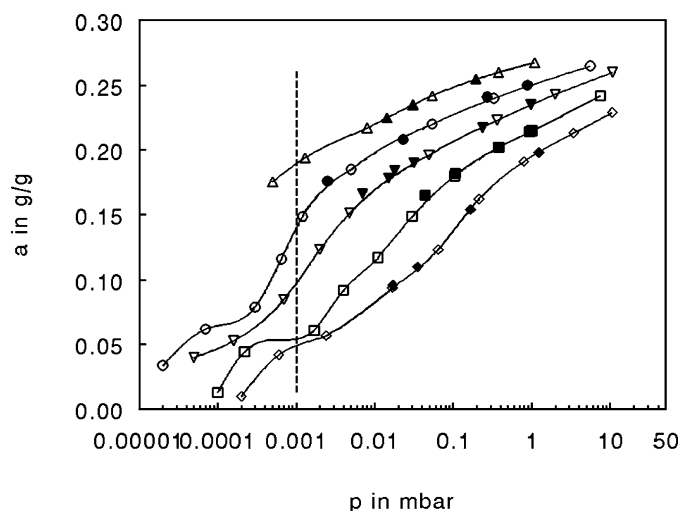


Fig. 1. Water adsorption isotherms for chabazite at 257, 275, 293, 313 and 333 K; filled symbols denote desorption, the dashed line indicates the relative water pressure on the martian surface.

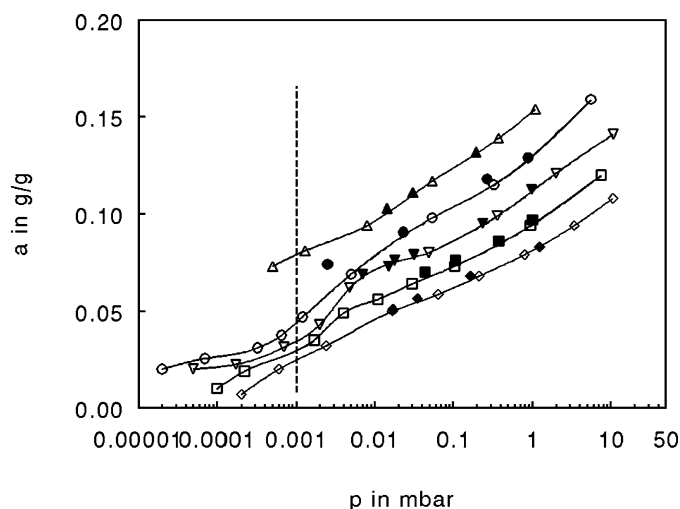


Fig. 2. Water adsorption isotherms for clinoptilolite at 257, 275, 293, 313 and 333 K; filled symbols denote desorption, the dashed line indicates the relative water pressure on the martian surface.

evidence of hysteresis between the ad- and desorption isotherm branches.

Water adsorption isotherms for montmorillonite and nontronite are shown in Figs. 3 and 4 over the same temperature and pressure range as Figs. 1 and 2. Compared with the zeolites, the isotherms for clays are shifted towards higher equilibrium pressures, indicating a lower strength of interaction of the water in the void volume of the montmorillonite and nontronite (the interlayer region). In this case lower temperatures are required for adsorption of similar amounts of water. In contrast to the zeolites, these smectites show a more (nontronite) or less (montmorillonite) pronounced hysteresis loop between the ad- and desorption branch of the isotherms. This behavior is well known and is due to structural changes (*d*-spacing) during the hydration and dehydration process, essentially phase transitions which is well documented by XRD experiments and is not a question of kinetics (see Chipera et al., 1997).

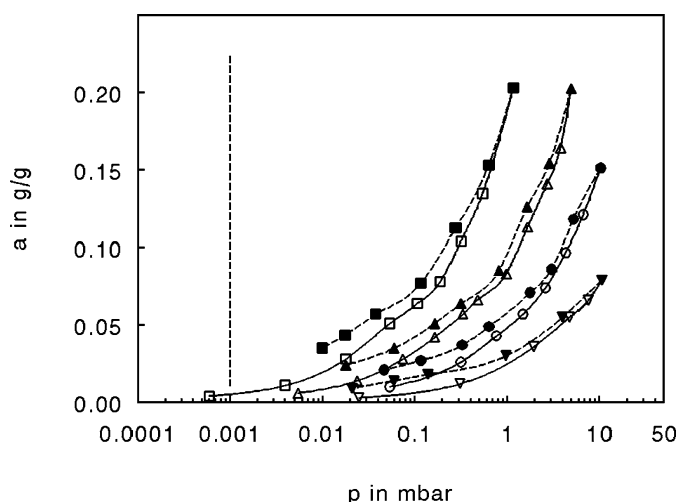


Fig. 3. Water adsorption isotherms for montmorillonite at 257, 275, 293 and 313 K; filled symbols denote desorption, the dashed line indicates the relative water pressure on the martian surface.

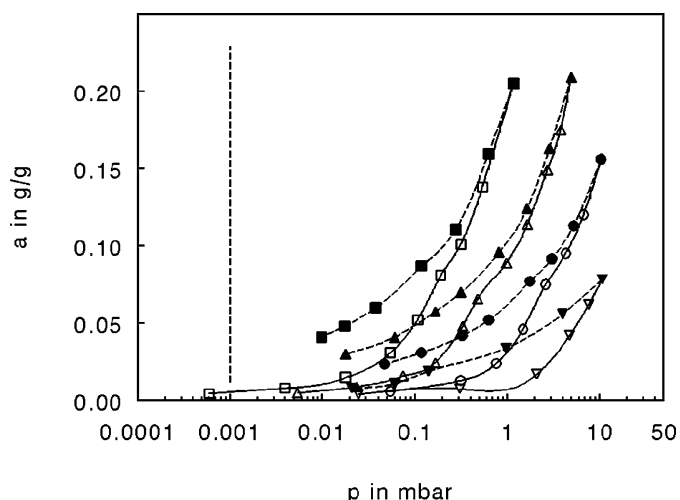


Fig. 4. Water adsorption isotherms for nontronite at 257, 275, 293 and 313 K; filled symbols denote desorption, the dashed line indicates the relative water pressure on the martian surface.

Figs. 5–8 summarize the results of the application of the Dubinin equation to the measured isotherm data for zeolites and smectites. For practical reasons the data are presented as isobars for water partial pressures of 0.1, 0.01, 0.001 and 0.0001 mbar and over the temperature range of 193–333 K, consistent with climatic data at the martian surface in equatorial latitudes between $\pm 45^\circ$ and diurnal and seasonal differences in temperatures. The experimental isotherm data revealed that porous minerals remain hydrated even at very low partial pressures of water expected on Mars. However, changes in water content of the different minerals can be determined directly from the isobars if, at a certain partial water pressure (for instance 0.001 mbar), the surface temperature changes due to seasonal influence or time of day (if fast enough).

Thus, chabazite (see Fig. 5) remains partially hydrated in equilibrium with the martian atmosphere even at a relatively high temperature of 293 K. The same is true for clinoptilolite

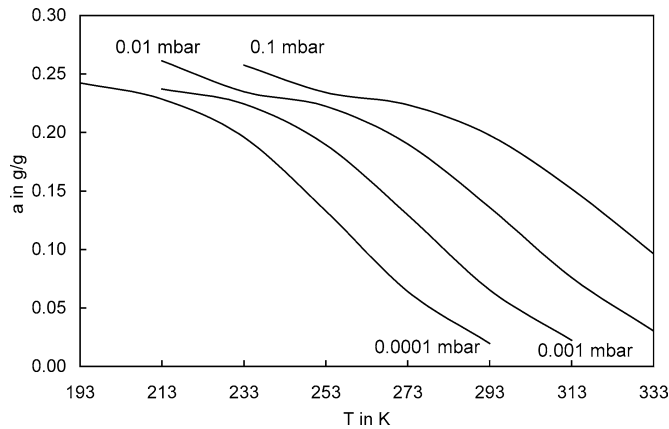


Fig. 5. Water adsorption isobars for chabazite at 0.0001, 0.001, 0.01 and 0.1 mbar in the temperature range 333–193 K calculated from the measured isotherm data.

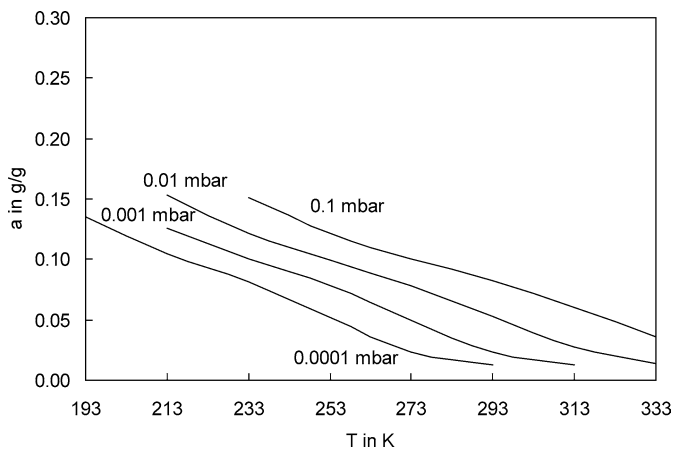


Fig. 6. Water adsorption isobars for clinoptilolite at 0.0001, 0.001, 0.01 and 0.1 mbar in the temperature range 333–193 K calculated from the measured isotherm data.

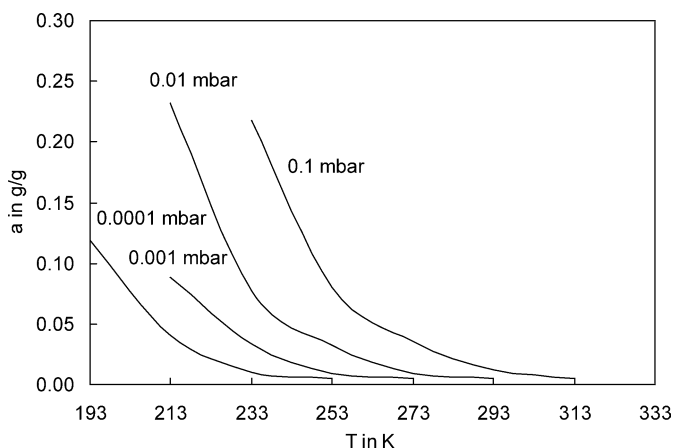


Fig. 7. Water adsorption isobars for montmorillonite at 0.0001, 0.001, 0.01 and 0.1 mbar in the temperature range 333–193 K calculated from the measured isotherm data (adsorption branch).

(Fig. 6). The changes with temperature are more or less continuous. This is not the case for the smectites. Furthermore, as mentioned above, smectites such as nontronite (Fig. 8) are only weakly hydrated at 293 K but progressively hydrate as tempera-

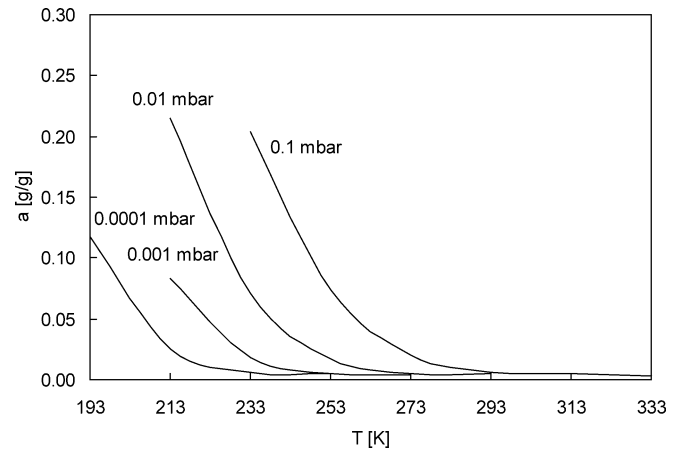


Fig. 8. Water adsorption isobars for nontronite at 0.0001, 0.001, 0.01 and 0.1 mbar in the temperature range 333–193 K calculated from the measured isotherm data (adsorption branch).

Table 1

Results of the TG/DSC measurements: sorption capacities/dehydrated amounts (a) and integral molar heats of desorption (dehydration) (Q_{int}) of water for zeolites, smectites ($p/p_s = 0.3$), and Mg- and Ca-sulfates

Material	a (g/g)	Q_{int} (kJ/mol)
Chabazite	0.270	73.6
Clinoptilolite	0.090	70.8
Nontronite	0.230	63.3
Montmorillonite	0.173	64.6
MgSO ₄ ·7H ₂ O	1.052	58.9
MgSO ₄ ·6H ₂ O	0.936	59
MgSO ₄ ·H ₂ O	0.183	85
CaSO ₄ ·2H ₂ O	0.263	64.9

ture decreases to $T < 253$ K (in adsorption mode). During desorption (dehydration), however, it is necessary to switch from the 0.001 to the 0.01 isobar to obtain the adsorbed amount as a result of the large amount of hysteresis (see Fig. 4). Nontronite would be more hydrated (~2.5 wt% at 253 K), increasing to ~10 wt% at 233 K if we assume that the process started with the fully hydrated material after crystallization in a wet period on Mars billion years ago. In other words the hydration state of nontronite (adsorption or desorption branch of the isotherm) has theoretically the potential to provide information on the history of the material. Nontronite remains on the desorption branch, independent of temperature change, if it began fully hydrated. Only fully dehydrated material hydrates along the adsorption branch because of the structure changes mentioned above.

The potential list of hydrated minerals in the martian regolith is large, among them a variety of different sulfates (Gendrin et al., 2005; Fialips et al., 2005). Therefore, we compare in Table 1 the TG and DSC data for chabazite, clinoptilolite, nontronite and montmorillonite with data for several sulfate minerals to obtain information on the stability of the sulfate hydrates. The mass losses (desorbed/dehydrated amounts of water) range between 0.17 and 1 g/g dry mineral and correspond well with values determined by the isotherm measurements for zeolites and clays and the molar water content of the sulfates.

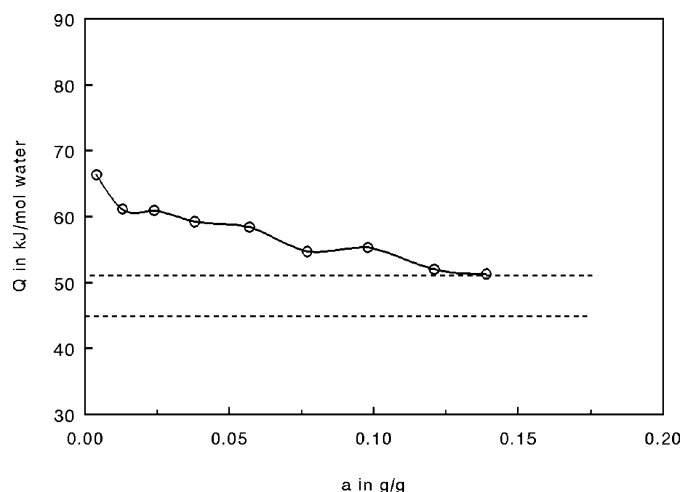


Fig. 9. Differential molar heats of adsorption as function of the adsorbed amount for water/nontronite at 303 K; dashed lines indicate the heat of vaporization of water and the heat of sublimation of water ice.

A comparison of the integral heats of desorption (last column in Table 1) is interesting because these values allow an estimate of the stability of the hydrated phases under certain condition of temperature and pressure (see Möhlmann, 2004). The zeolites chabazite and clinoptilolite remain at least partially hydrated over the measured temperature range of the isotherms, whereas the smectites (nontronite and montmorillonite) do not. Accordingly, the integral heats of desorption are lower by about 10 kJ/mol, although this is still higher than the enthalpy of sublimation of ice (50.87 kJ/mol).

Fig. 9 shows, as an example, the heat curve (differential molar heats of adsorption as function of the adsorbed amount) for nontronite in comparison with the value of the heat of vaporization of water and the heat of sublimation of ice. From this figure can be concluded that at lower loadings typical of nontronite ($a < 0.1$ g/g) the heats of adsorption are significantly higher than the heat of sublimation of ice. Consequently, at least partially hydrated nontronite should be more stable than water ice.

The integral heats of dehydration of the sulfates (see Table 1) depend on the hydration state of the sulfate mineral and range between 59 and 85 kJ/mol. These values are all higher than the heat of sublimation of ice, and the magnesium sulfate should be stable (at least as monohydrate) under the temperature and vapor pressure conditions on the martian surface. These results show that water can exist as adsorption water or hydrate water in equilibrium with the martian atmosphere in regions of the upper martian surface where water ice has disappeared via sublimation. These findings are consistent with the Mars Odyssey data and the results of the OMEGA/Mars Express mission.

The NMR results (Figs. 10 and 11) provide information on the mobility of the hydrate water in these minerals (Yesinowski et al., 1988). According to Yesinowski et al., structurally isolated water groups in minerals such as gypsum yield sharp peaks with a characteristic dipolar sideband pattern extending over ~ 100 kHz. In contrast, isotropically mobile water in fluid inclusions gives rise to single sharp peaks without spinning side

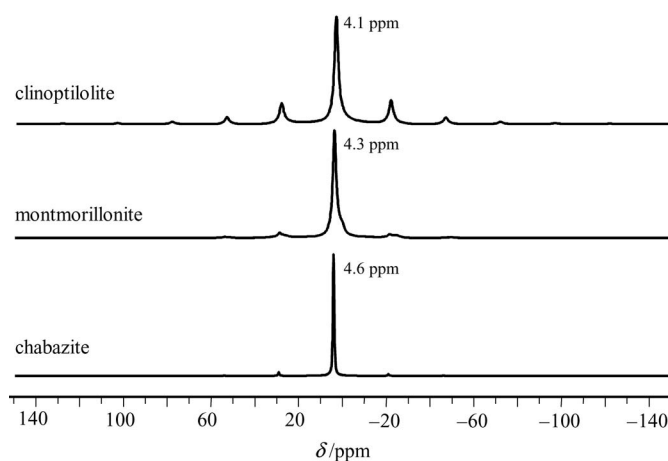


Fig. 10. ^1H MAS MNR spectra of chabazite, clinoptilolite and montmorillonite at room temperature.

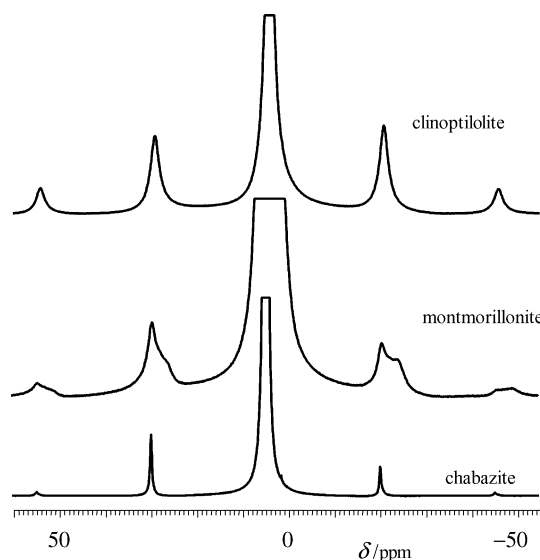


Fig. 11. Details of the ^1H MAS MNR spectra of the chabazite, clinoptilolite and montmorillonite at room temperature.

bands, as can be seen for chabazite with a sharp peak at 4.6 ppm (Fig. 10) and only hints of spinning side bands (see Fig. 11). Montmorillonite shows a broader signal with some spinning side bands and clinoptilolite shows the pattern for less-mobile water. Unfortunately, nontronite is not suitable for NMR experiments because of its iron content but it is expected to be similar to montmorillonite. The NMR spectra suggest that the water in chabazite and in smectite is at least partially mobile. Most of the water in chabazite and about 80% of that in montmorillonite is mobile water (on the time scale of the NMR experiment, 10 μs) and the remaining amount is more tightly bound. Clinoptilolite contains about 25% of its water in a mobile state whereas the majority of the water is more tightly bonded.

Measurements of the intracrystalline self-diffusion of water in A-type zeolites using the NMR pulsed-field gradient technique (by Kärger et al., 1989) show that the mobility of the adsorbed water can be quite high and depends on different parameters such as the type of zeolite, the kind of cations, the

adsorbed amount and the number of “frozen” water molecules. For an Si-rich A-type zeolite (ZK-4) the self-diffusion coefficient for the adsorbed water is $5 \times 10^9 \text{ m}^2 \text{ s}^{-1}$ at 250 K and to about $5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 200 K, which is only one to two orders of magnitude lower than the corresponding coefficients for liquid water at room temperature. Thus, the presence of adsorption water and its mobility in these porous minerals might be important for adsorption-water-triggered chemistry and hypothetical exobiological activity on Mars (Möhlmann, 2004).

4. Conclusions

- Based on the results of our laboratory studies, components of the martian soil identified by the OMEGA team, including smectites, Mg-sulfates, Ca-sulfate, and zeolites, can remain hydrated at water vapor pressures <0.01 mbar and temperatures between 333–257 K.
- The existence of pronounced water adsorption hysteresis in smectite due to reversible structural changes suggests the possibility of deciphering information on the past history of clay-bearing deposits on Mars.
- Results of NMR measurements of adsorbed water in porous minerals suggest that adsorption water remains mobile in some minerals at temperatures down to 200 K.
- The presence of hydrated minerals and the (partial) mobility of their adsorption water in the upper layer of the martian surface might be important for adsorption-water-triggered chemistry and hypothetical exobiological activity on Mars.

Acknowledgments

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