



## Stability of hydrated minerals on Mars

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[1] The validity of recent identification of various hydrated minerals (kieserite, gypsum, hexahydrite, nontronite, chamosite, and montmorillonite) on Mars was assessed by exposing these minerals to simulated Martian surface conditions of atmospheric composition and pressure, temperature, and ultraviolet light irradiation. When exposed to such conditions the hydrated minerals exhibit in general, greater losses of interlayer H<sub>2</sub>O than structural OH. Minerals such as gypsum that contain structural H<sub>2</sub>O are more resistant to H<sub>2</sub>O loss than phyllosilicates. The partial loss of OH in some of the phyllosilicates is not accompanied by a measurable and systematic change in the wavelength position or intensity of metal-OH absorption bands. The characteristic absorption features that allow for identification of these minerals on Mars may be reduced in intensity, but are nevertheless largely preserved.  
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### 1. Introduction

[2] The recent discovery of a number of distinct hydrated minerals on Mars [Gendrin *et al.*, 2005; Langevin *et al.*, 2005; Poulet *et al.*, 2005] provides new insights into the geological and climatic history of the planet. The presence of hydrated minerals likely indicates that conditions in the past were more conducive to the presence of liquid water at or near the surface. These detections are based on the presence of presumed unique absorption bands in spectra obtained by the Mars Express OMEGA spectrometer in the 1.0–2.5  $\mu\text{m}$  wavelength range. One issue that has been unresolved is whether these characteristic absorption bands would persist under current Martian surface conditions. If they are ephemeral, it would imply that these minerals have only recently been exposed at the surface. A number of the hydrated minerals were exposed to simulated Mars surface

conditions in order to assess their stability to current Mars surface conditions.

[3] The OMEGA/Mars Express hyperspectral imager has detected the presence of kieserite, an unspecified polyhydrated sulfate, gypsum, nontronite, chamosite, and montmorillonite on the surface of Mars [Gendrin *et al.*, 2005; Langevin *et al.*, 2005; Poulet *et al.*, 2005]. The OMEGA identifications were based on similarities of the OMEGA spectra to laboratory spectra of candidate minerals acquired under ambient terrestrial conditions. Spectral reflectance studies of minerals exposed to simulated Mars surface conditions are limited [Bishop and Pieters, 1995] but suggest that significant spectral changes may occur in hydrated minerals when they are exposed to pressure of a few Pa or less. Spectral reflectance studies of minerals exposed to more Mars-like ( $\sim 660$  Pa) pressures are lacking. Non-spectral studies show that compositional and structural changes accompany exposure of some hydrated sulfates to such conditions, and that ultraviolet irradiation may also lead to changes in composition, structure, and iron oxidation state [Braterman *et al.*, 1983; Bish *et al.*, 2003; Vaniman *et al.*, 2004; Chipera *et al.*, 2005; Vaniman and Chipera, 2006; Vaniman *et al.*, 2006]. In addition, seasonal changes in bound water abundances in surficial minerals have been detected in Mars orbital data [Kuzmin *et al.*, 2004].

### 2. Experimental Conditions

[4] To determine the robustness of the hydrated mineral identifications made on Mars to date, we subjected kieserite, gypsum, hexahydrite, nontronite, chamosite, and montmorillonite to simulated Mars surface conditions of atmospheric pressure and composition, and ultraviolet (UV) light regime for periods of up to 47 days. Experimental conditions were changed approximately every 10 days in order to better isolate the relative importance of atmospheric pressure and UV irradiation on mineral stability. Such spectroscopy-based studies are complementary to similar X-ray based investigations that monitor structural changes accompanying exposure of minerals to low atmospheric pressures [Vaniman *et al.*, 2004].

[5] The experiments were conducted at the University of Winnipeg [Cloutis *et al.*, 2006a] using a Mars environment simulation chamber (mini-ME) [Craig *et al.*, 2001]. The chamber allowed us to expose up to nine samples simultaneously to pressures as low as 1 Pa. The temperature of the sample holder (in thermal contact with the samples) was kept to between 12 and 26°C with a cold water circulation system. It should be noted that we were only able to monitor the temperature of the wall of the environment chamber and not the surfaces of the powdered samples, whose temperatures we were most interested in monitoring. UV irradiation utilized two 25 W deuterium lamps and one day of irradiation

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was calculated as being roughly equivalent to one decade on Mars. The samples were exposed sequentially to 10 days each of 660 Pa CO<sub>2</sub>, 660 Pa CO<sub>2</sub> + UV irradiation, and between 1.0 and 2.7 Pa CO<sub>2</sub>, with the exception of the first run which exposed the samples to 14 days of 660 Pa CO<sub>2</sub>, 9 days of 660 Pa CO<sub>2</sub> + UV irradiation, and 24 days of 1.0 Pa (the ultimate lower pressure was a function of the capability of the vacuum system during a particular experimental run). A constant inflow of CO<sub>2</sub> was passed through a Drierite<sup>®</sup> assembly and was balanced against outflow to maintain a constant pressure in the chamber and facilitate removal of any liberated water from the samples for the 660 Pa runs. For the 1.0–2.6 Pa runs, the CO<sub>2</sub> inflow was shut off but the vacuum pump was left running.

[6] Mini-ME was equipped with a 10 mm thick sapphire window that allowed for UV irradiation to as low as 200 nm as well as spectral data acquisition. The 200 nm lower irradiation limit is roughly equivalent to the lower level of transparency of the Mars atmosphere [Kuhn and Atreya, 1979; Cockell et al., 2000]. Reflectance spectra were acquired using an Analytical Spectral devices Field Spec Pro HR spectrophotometer and an 11 W quartz tungsten halogen bulb incident light source. The instrument acquires data between 0.35 and 2.5 μm with a spectral resolution of between 2 nm (near 0.35 μm) and 7 nm (near 2.5 μm) and spectral sampling at 1 nm intervals. Spectra were acquired at incidence and emission angles of 0° using a bifurcated reflectance probe, and 2000 spectra were averaged to reduce signal to noise. The fibers in the probe each have a 25° angle of divergence, thus providing overlapping fields of illumination and emission. Consequently, incidence and emission angles vary from 0–12.5°. Reflectance spectra were measured relative to a halon standard located in the same sample disk as the mineral samples. The halon showed no spurious spectral features relative to Spectralon<sup>®</sup> and the data were corrected for irregularities in halon's absolute reflectance in the 2–2.5 μm region. Halon has no measurable temperature-dependent spectral variations over the range of temperatures (12–25°C) and spectral range (0.35–2.5 μm) used in these experiments. Wavelength calibration was monitored through periodic measurements of an HoO-doped Spectralon<sup>®</sup> standard. Spectra were measured for <45 μm sized dry sieved mineral fractions. The resulting spectra were resampled to match the OMEGA bands. Unratioed OMEGA spectra were used for comparisons to the sulfates, whereas OMEGA spectra ratioed to a spectrally neutral region were used for comparison to the phyllosilicate spectra.

[7] Scattering of incident light off the sapphire window and chamber walls resulted in loss of contrast due to scattering and reflection (the transmission function of the sapphire window is essentially constant across the 0.35–2.5 μm interval). This caused mineral absorption bands to be shallower than in the spectra of the same minerals acquired outside the environment chamber. However this scattered light was largely spectrally neutral and raised overall reflectance; it did not add any spurious spectral features to the data or significantly change overall spectral slopes.

### 3. Results

[8] The results of our experimental runs are presented below for each mineral. For the sake of clarity, we present

only the spectra acquired at the start of each run, at the end of the 660 Pa segment, at the end of the 660 Pa + UV irradiation segment, and at the end of the few Pa segment. In addition, the discussion is largely focused on absorption features identified in OMEGA spectra as being particularly characteristic, and hence used for identification, of a specific mineral.

#### 3.1. “Kieserite”

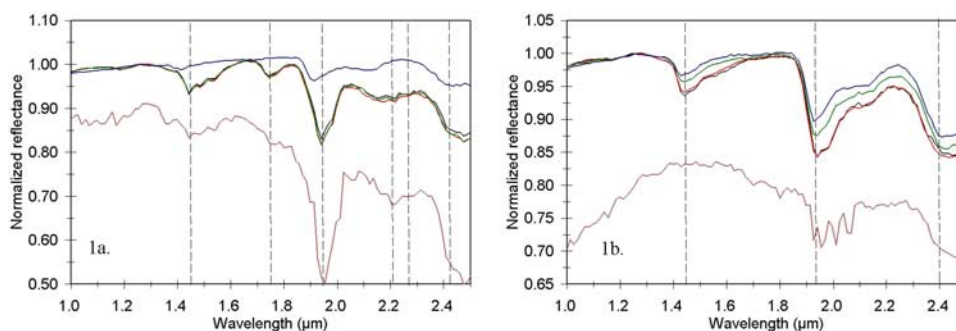
[9] Kieserite is a hydrated sulfate (nominally MgSO<sub>4</sub> • H<sub>2</sub>O) with an as-yet incompletely understood stability field [Vaniman et al., 2004; Marion and Kargel, 2005] whose presence on Mars was suggested based upon the Mars Express OMEGA spectrometer data [Gendrin et al., 2005]. Our attempts to measure the spectral changes accompanying exposure of kieserite to Mars surface conditions were thwarted by apparent hydration of our sample between the time it was characterized as being kieserite by X-ray diffraction and our experimental run. This is not unexpected as kieserite stability is sensitive to humidity [Vaniman et al., 2004, 2006], and the spectra of presumed kieserite as measured by different investigators are also variable [Dalton, 2003; Bonello et al., 2005; Gendrin et al., 2005; Cloutis et al., 2006b]. As a result we were unable to confidently compare our experimental run spectra to the OMEGA kieserite spectra.

#### 3.2. Gypsum

[10] Gypsum was identified in OMEGA spectra on the basis of absorption bands at 1.4, 1.75, 1.9, 2.21, 2.27, and 2.4 μm [Gendrin et al., 2005; Langevin et al., 2005]. We measured two samples of gypsum in our experimental runs on two separate occasions. In the first experiment, we achieved an ultimate lower pressure of 1.0 Pa, and in the second, 2.7 Pa. In both runs, no significant spectral changes occurred during the 660 Pa ± UV irradiation segments. Spectral changes only occurred when the pressure was reduced to 1.0 Pa but not 2.7 Pa (Figure 1a), resulting in a drastic reduction in band depths and the loss of characteristic bands at 1.45 and 1.75 μm, likely due to dehydration of the sample. The overall similarity of the ambient gypsum spectrum to the OMEGA spectra, particularly in terms of absorption band depths suggests that the gypsum detected by OMEGA in the polar dunes in Olympia Planitia has not suffered a significant degree of dehydration or very low pressure (a few Pa) excursions [Vaniman and Chipera, 2006]. The OMEGA spectra are best matched by our gypsum spectra rather than by bassanite, a more water-poor calcium sulfate (2CaSO<sub>4</sub> • H<sub>2</sub>O) [Crowley, 1991], or anhydrite (CaSO<sub>4</sub>) [Cloutis et al., 2006b].

#### 3.3. Hexahydrate

[11] The nature of the polyhydrated sulfate on Mars has not been more precisely identified, as a number of polyhydrated sulfates exhibit broadly similar spectral features [Cloutis et al., 2006b]. This OMEGA spectral type is characterized by absorption features near 1.45, 1.95, and 2.4 μm with plateau-like longer wavelength wings and was matched to epsomite, a seven-hydrated Mg-sulfate [Gendrin et al., 2005]. We exposed a number of polyhydrated sulfates to Mars surface conditions and here present the results for hexahydrate as an example of the spectral changes experienced by polyhydrated sulfates in general (Figure 1b).



**Figure 1.** 1.0–2.5  $\mu\text{m}$  reflectance spectra of (a) gypsum and (b) hexahydrite measured at start of experimental run (black), after 10 days (hexahydrite) or 14 days (gypsum) of exposure to 660 Pa  $\text{CO}_2$  (red), after an additional 10 days (hexahydrite) or 9 days (gypsum) of 660 Pa  $\text{CO}_2$  plus UV irradiation (green), and after an additional 10 days (hexahydrite) or 24 days (gypsum) at 1.0 Pa  $\text{CO}_2$  (blue). The OMEGA spectra used for comparison are shown in brown. All spectra have been normalized to 1 at 1.25  $\mu\text{m}$  and the OMEGA spectra have been linearly vertically offset for clarity. The vertical dashed lines correspond to wavelengths identified by the OMEGA Team as being significant for identification of the particular mineral under discussion.

Increasing exposure time causes a reduction in depths of the features near 1.45 and 1.95  $\mu\text{m}$ , as well as a flattening of the longer wavelength wings and the broad absorption feature in the 1.7  $\mu\text{m}$  region. In particular, the absorption features near 1.9  $\mu\text{m}$  becomes progressively shallower, consistent with a reduction in water content [Dalton, 2003]. The spectral changes mimic those accompanying heating of polyhydrated sulfates [Bonello *et al.*, 2005]. These partially dehydrated sulfates present an overall appearance that is similar to the OMEGA spectra, but without losing their characteristic features. The alteration of hexahydrite to a different phase (based on changes in the shape of its spectrum) is consistent with the results of other investigators, where hexahydrite altered to an amorphous state after 33 hours of exposure to 130 Pa pressures [Vaniman *et al.*, 2005]. It appears that the hexahydrite was stable at 660 Pa, but that dehydration was initiated or accelerated by the addition of UV irradiation, and further accelerated by reduction of atmospheric pressure to 1.0 Pa.

### 3.4. Nontronite

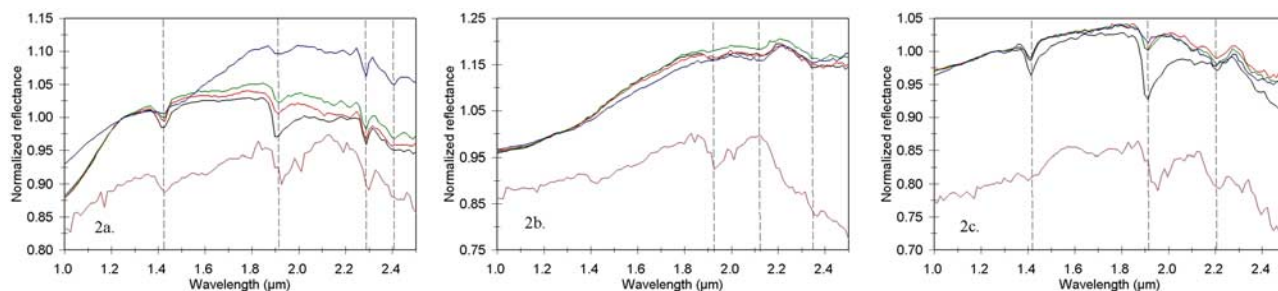
[12] The identification of nontronite on Mars was largely based on absorption features at 1.41, 2.29 and 2.40  $\mu\text{m}$ , as well as overall spectral shape, features that are characteristic of Fe-rich smectites such as nontronite [Poulet *et al.*, 2005]. Exposure of nontronite to simulated Mars surface conditions results in a number of measurable changes, including reductions in depths of absorption bands in the 1.41 and 1.9  $\mu\text{m}$  regions (Figure 2a). Absorption bands at 2.29 and 2.40  $\mu\text{m}$  regions are largely unaffected. At the lowest pressures, the shorter wavelength interval (<1.4  $\mu\text{m}$ ) becomes flatter, similar to the OMEGA spectra, but all of the characteristic absorption features are preserved. There are slight differences between the OMEGA and laboratory spectra in terms of the wavelength positions of the 1.9 and 2.29  $\mu\text{m}$  bands (on the order of 10–15 nm) but these differences are not significant enough to obviate the identification of nontronite. These results suggest that Fe-rich smectites are stable under current Mars surface conditions, and hence spectrally detectable, consistent with the data and simulations on smectite [Bish *et al.*, 2003].

### 3.5. Chamosite

[13] Chamosite was identified in OMEGA spectra on the basis of absorption features at 1.41 and 2.35  $\mu\text{m}$  and overall spectral shape [Poulet *et al.*, 2005]. We use the term chamosite here to mean an Fe-rich chlorite. Our chamosite spectrum differs from the laboratory spectrum [Poulet *et al.*, 2005] in having more subdued absorption bands (Figure 2b). However its overall spectral shape is similar. Exposure to 660 Pa  $\pm$  UV irradiation does not appreciably affect the spectrum. Exposure to 1.3 Pa causes the 1.91  $\mu\text{m}$  feature to essentially disappear but the 2.35  $\mu\text{m}$  absorption band is preserved. The 2.13  $\mu\text{m}$  feature is a local maximum but is not characteristic of a specific cation or mineral. These results suggest that chamosite is stable under current Mars atmospheric pressures (but not necessarily current atmospheric water vapor pressures) but excursions to pressures of a few Pa may cause the rapid loss of one of its characteristic spectral features (at 1.41  $\mu\text{m}$ ). It should be noted that absorption bands characteristic of iron oxidation state occur below 1  $\mu\text{m}$  and this wavelength range is not available in the current OMEGA data set.

### 3.6. Montmorillonite

[14] Montmorillonite was identified in OMEGA spectra on the basis of absorption bands at 1.41, 2.21, and 2.35  $\mu\text{m}$ , features characteristic of Al-rich phyllosilicates [Poulet *et al.*, 2005]. Our ambient montmorillonite spectrum exhibits all of these features (Figure 2c). Upon exposure to 660 Pa and 2.7 Pa pressures, the 1.41 and 2.21  $\mu\text{m}$  features, as well as the 1.91  $\mu\text{m}$  absorption band, become progressively shallower but are still apparent. The long wavelength wings of both the 1.91 and 2.21  $\mu\text{m}$  features also become flatter, similar to the OMEGA spectrum. The stability of the 2.21  $\mu\text{m}$  feature was also noted by others [Bishop and Pieters, 1995] in low-pressure and -temperature experiments. The position of the 1.91  $\mu\text{m}$  absorption band differs between the laboratory and OMEGA spectra, but this feature is not particularly diagnostic of a specific phyllosilicate. The 2.35  $\mu\text{m}$  feature seems to disappear during UV irradiation and reappear during the lowest pressure exposure. However this feature is weak and its apparent disappearance is likely due



**Figure 2.** 1.0–2.5  $\mu\text{m}$  reflectance spectra of (a) nontronite, (b) chamosite, and (c) montmorillonite measured at start of experimental run (black), after 14 days (nontronite) or 10 days (chamosite, montmorillonite) of exposure to 660 Pa  $\text{CO}_2$  (red), after an additional 9 days (nontronite) or 10 days (chamosite, montmorillonite) of 660 Pa  $\text{CO}_2$  plus UV irradiation (green), and after an additional 24 days (nontronite) or 10 days (chamosite, montmorillonite) at 1.0 Pa  $\text{CO}_2$  (blue). The OMEGA spectra used for comparison are shown in brown. All spectra have been normalized to 1 at 1.25  $\mu\text{m}$  and the OMEGA spectra have been linearly vertically offset for clarity. The vertical dashed lines correspond to wavelengths identified by the OMEGA Team as being significant for identification of the particular mineral under discussion.

to individual measurement variance. These results suggest that montmorillonite retains its characteristic absorption features under current Mars surface atmospheric pressure and are consistent with the data and simulations on smectite [Bish *et al.*, 2003].

#### 4. Discussion

[15] These experimental results provide many useful insights into the stabilities of a number of hydrated minerals that have been identified on Mars, but they also raise a number of questions. The behavior of the gypsum sample when variously exposed to 1.0 or 2.7 Pa suggests that gypsum dehydration may be controlled more by partial pressure of  $\text{H}_2\text{O}$  than kinetics. This also leads into the question of whether exposing minerals to a few Pa levels of atmospheric pressure for a few days is a reasonable simulation of thousands or millions of years of exposure to 660 Pa pressures, as well as issues of reversibility of dehydration. In addition, we have not investigated the effects of temperature excursions on alteration kinetics [Chipera *et al.*, 2005]. Our experimental setup also did not allow us to actively influence relative humidity, which is a difficult parameter to control in low pressure environments (<http://www.vacuumlab.com>). Kinetic effects are known to play a role in the dehydration behavior of Ca- and Mg-sulfates [Vaniman and Chipera, 2006]. Kinetic effects and relative humidity are both important factors controlling the stability of hydrated Mg-sulfates [Feldman *et al.*, 2004; Vaniman *et al.*, 2004] and for many minerals there is likely a complex interplay of multiple factors [Hamad, 1976].

[16] The study results suggest that exposure to UV irradiation, equivalent to a few centuries of Mars surface exposure, does not appear to accelerate the dehydration process of the gypsum or phyllosilicates used in this study, or lead to the formation of other spectrally detectable phases. UV irradiation does however appear to accelerate the dehydration of the hexahydrate. Previous studies have suggested that UV radiation can photolyse  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  under a variety of conditions [Braterman *et al.*, 1983] and have a range of other effects on many minerals, at least in aqueous environments [Waite, 1990] – although our mate-

rials here are largely  $\text{Fe}^{3+}$ -bearing, apart from chamosite. Our results suggest that UV photolysis is not a major conversion factor for these minerals as no evident changes occurred in the region of  $\text{Fe}^{2+}$  absorption bands in the chamosite which contains 26 wt. %  $\text{Fe}_2\text{O}_3$  and 29 wt. %  $\text{FeO}$ . When calibrated lower wavelength ( $<1 \mu\text{m}$ ) OMEGA data become available, the oxidation state of iron-bearing minerals will become readily accessible. With the notable exception of the hexahydrate, ultraviolet irradiation does not appear to be an effective process for liberation of hydroxyl or water from minerals, consistent with the results of mass spectrometer-based measures of water/hydroxyl liberation from minerals subjected to ultraviolet irradiation [Yen *et al.*, 1999].

[17] While matching absorption features is a powerful technique for mineral identification, it should be noted that not all absorption features are equally valuable. Absorption bands attributable to water (in the 1.4 and 1.9  $\mu\text{m}$  regions) are usually of limited utility because a wide range of minerals may exhibit features in this region. In addition, it is unlikely that the OMEGA spectra sample a monomineralic target, and hence spectral contributions from additional phases are likely. Nevertheless judicious use of diagnostic absorption bands, ideally using multiple absorption bands and other spectral features such as spectral slopes, can result in robust mineral identifications.

[18] The fact that none of the minerals showed complete disappearance of pre-existing water/hydroxyl-related absorption bands is consistent with other experiments indicating that adsorbed and structural water would persist on the Martian surface under current conditions in many minerals [Jänchen *et al.*, 2005].

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