

# Stability of hydroxylated minerals on Mars: A study on the effects of exposure to ultraviolet radiation

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**Abstract.** The density and composition of the Martian atmosphere allow solar ultraviolet photons with wavelengths as short as 190 nm to reach the surface. We investigate the hypothesis that this UV radiation is capable of inducing the release of water from iron oxyhydroxide minerals resulting in the formation of oxide phases. These experiments, which utilize a quadrupole mass spectrometer to monitor the water vapor pressure above mineral samples during cyclic exposure to ultraviolet radiation, offer 5 to 6 orders of magnitude greater sensitivity than previous attempts to establish and quantify this process. We find no evidence that UV photons are capable of liberating OH from the crystal lattice of minerals, and we set a minimum ultraviolet radiation-induced dehydroxylation time of  $10^8$  years for removal of this structural OH from mineral particles at the Martian surface. The overturning timescales for surface fines are likely to be shorter than this lower limit for exposure time. Thus we conclude that UV-stimulated dehydroxylation is not a significant process at the Martian surface and that iron oxyhydroxides, if formed during an earlier water-rich environment, should still be found on Mars today. The lack of clear evidence for iron oxyhydroxides at the Martian surface further suggests that Mars' surface was never warm and wet for a long enough period of time for Earth-like weathering to have occurred.

## 1. Introduction

### 1.1. Ferric Minerals on Mars

The visible color of the Martian surface has traditionally been attributed to the presence of ferric iron in the soil [e.g., Soderblom, 1992]. Charge transfer between  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  strongly absorbs in the blue and near-ultraviolet regions of the spectrum giving the planet its characteristic color. Recent data from the Mars Global Surveyor Thermal Emission Spectrometer show a region interpreted to be crystalline hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) approximately 300 km in diameter near the equator at  $\sim 5^\circ\text{W}$  [Christensen *et al.*, 1999]. In situ data from the Mars Pathfinder camera indicate that iron minerals may also be responsible for a 930 nm absorption in some soils [Smith *et al.*, 1997]. A ferric component was also inferred from the Viking magnetic properties experiments which indicated the presence of 1% to 7% of a highly magnetic mineral phase, likely maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), in the Martian soil [Hargraves *et al.*, 1977]. These Viking results are supported by the Pathfinder data which suggest that most dust particles contain about 6% maghemite [Hviid *et al.*, 1997]. On a more global scale, Morris *et al.* [1993] suggest that the primary

mineral phase responsible for the pigment of bright soils and dust on Mars is likely nanocrystalline hematite.

Understanding the origin of the iron oxides would significantly advance our understanding of the surface weathering processes and the climate history of Mars. A commonly viewed means of producing hematite and maghemite is through the dehydroxylation of goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ), respectively [Morris *et al.*, 1998]. These polymorphs of FeOOH are common minerals on Earth and typically form as precipitates after aqueous dissolution and oxidation of ferrous iron. Some weathering models indicate that FeOOH should be a product of interactions between liquid water and silicate minerals on Mars [Burns, 1993], but convincing evidence for the presence of goethite or lepidocrocite on Mars is still absent. Hence either a mechanism for converting FeOOH to  $\text{Fe}_2\text{O}_3$  has been active at the Martian surface or there is an alternative process for forming hematite and maghemite, possibly one that does not involve the action of liquid water. In this paper we explore and reject the possibility that ultraviolet radiation incident upon the Martian surface can induce the dehydroxylation of FeOOH, thus accounting for its apparent absence now. Alternative, nonaqueous means of producing iron oxides and other nanocrystalline components in the Martian soil have been suggested elsewhere [Yen and Murray, 1998; Banin *et al.*, 1997]. Together these ideas support the possibility that Mars' surface was never warm and wet for a long enough period of time for Earth-like weathering to have occurred.

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## 1.2. Ultraviolet Radiation at the Martian Surface

The composition and pressure (5.6 mbar global annual average) of the Martian atmosphere allows solar ultraviolet photons to reach the surface. Models developed by *Kuhn and Atreya* [1979] indicate that under present climatic conditions, absorption by ozone centered at  $\sim 255$  nm allows  $10^{-2}$  of incident solar photons to reach the surface (as compared to  $10^{-34}$  for the Earth). They also indicate that wavelengths as short as 190 to 200 nm (energies of up to  $\sim 6.5$  eV) can penetrate the carbon dioxide atmosphere to the surface. Dust suspended in the atmosphere would receive even more UV radiation because of the shorter atmospheric path to these particles. In addition, during periods of low obliquity, the atmospheric pressure could be as low as 0.3 mbar [*Ward et al.*, 1974] and would result in a greater amount of ultraviolet flux at the surface.

## 1.3. Possible Effects of UV

What effects might this UV flux have on the Martian surface materials? *Andersen and Huguenin* [1977] proposed that ultraviolet radiation is capable of dehydroxylating minerals. According to their abstract, photons with wavelengths shorter than 280 nm release  $\text{H}_2\text{O}$  (g) from goethite by ejecting  $\text{OH}^-$  groups which subsequently combine with  $\text{H}^+$  from nearby sites. We believe that this mechanism for mineral decomposition is unlikely given well-documented experiments indicating insufficient kinetic energy for ejecting  $\text{OH}^-$  fragments from water adsorbed on surfaces with excitation up to 10 eV (ejection from the substrate itself is even less plausible) [e.g., *Simpson et al.*, 1998]. Furthermore, *Morris and Lauer* [1981] found no UV dehydroxylation effects on goethite ( $\alpha\text{-FeOOH}$ ) or lepidocrocite ( $\gamma\text{-FeOOH}$ ) in exposures equivalent to 10 to 100 years on the Martian surface and attributed the earlier findings to sample heating rather than ultraviolet radiation-induced effects. Work by *Muhkin et al.* [1996], however, demonstrated that ultraviolet photons are capable of decomposing carbonates and sulfates releasing  $\text{CO}_2$  and  $\text{SO}_2$ , respectively, suggesting that photo-induced alterations of solid surfaces can, in fact, be a relevant process at the Martian surface. Thus the role of UV radiation in the dehydroxylation of minerals on Mars warrants more detailed study.

## 1.4. Experiments

We have developed a series of experiments that offer 5 to 6 orders of magnitude greater sensitivity than the *Morris and Lauer* [1981] study of UV-induced decomposition of Martian minerals. In this study we do not observe any effects of ultraviolet radiation on the OH in the crystal structure of iron oxyhydroxides. On the basis of our experiments we calculate a minimum exposure time of  $10^8$  years for UV-induced dehydroxylation of goethite or lepidocrocite at the Martian surface. This minimum value is set by the sensitivity limits of our experiment, and the actual required exposure times may be much longer. Thus we conclude that UV-induced dehydroxylation is not a plausible explanation for the apparent absence of goethite or lepidocrocite on Mars. Instead, these minerals may never have formed at the Martian surface suggesting that the ferric color is derived from a weathering history that does not involve liquid water.

## 2. Experiment Description

### 2.1. Apparatus

A block diagram of our experimental setup is shown in Figure 1. Samples were placed in a vacuum chamber which was

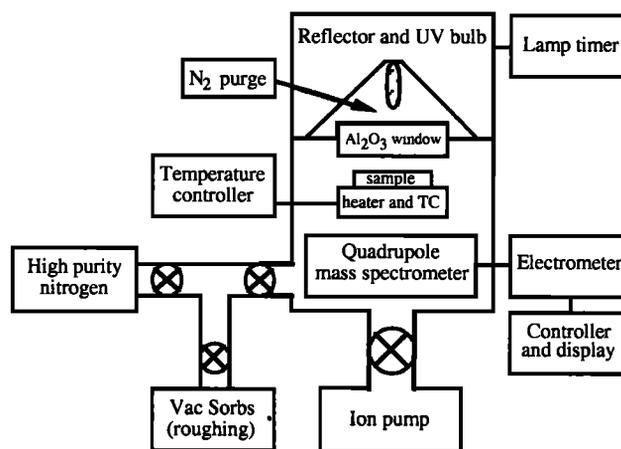


Figure 1. Block diagram of experimental apparatus.

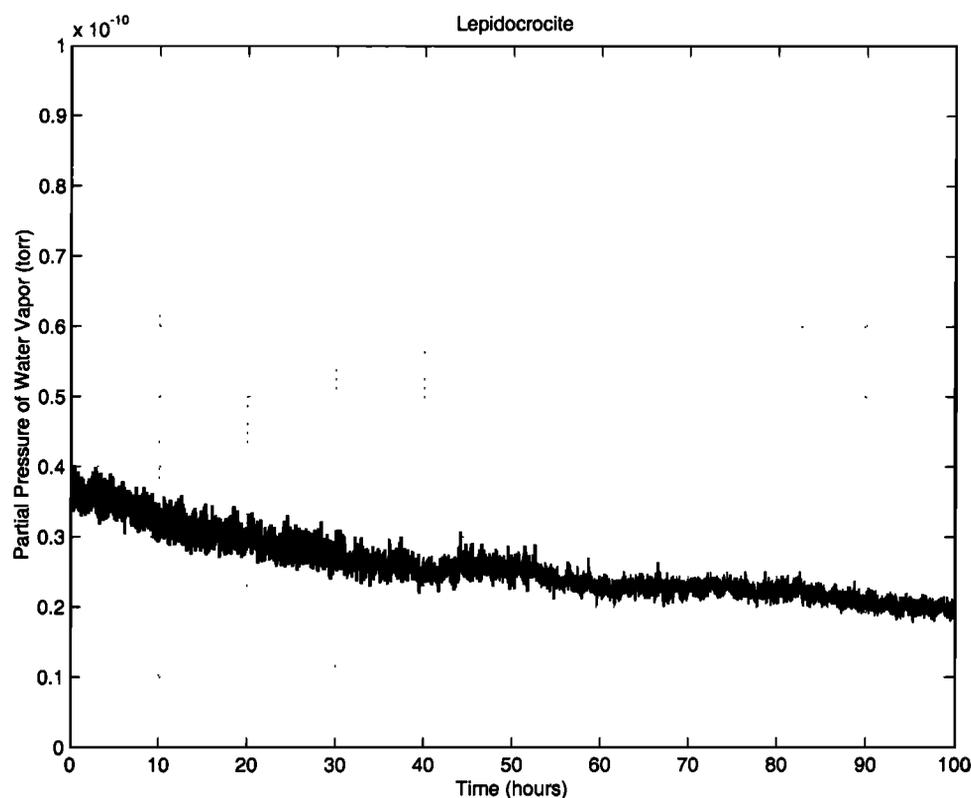
maintained at pressures of approximately  $10^{-10}$  torr using an ion-sputtering pump. An AMETEK Dycor quadrupole mass spectrometer with a Faraday cup and electron multiplier was used to monitor the gas phase species in the chamber. A mercury vapor lamp and reflector assembly external to the vacuum chamber was maintained under a nitrogen purge and radiated the sample with ultraviolet photons through an  $\text{Al}_2\text{O}_3$  window. These samples were located 1.5 cm beneath the window and, when the lamp was on, were exposed to approximately  $5.0$   $\text{mW}/\text{cm}^2$ ,  $200$   $\mu\text{W}/\text{cm}^2$ , and  $150$   $\mu\text{W}/\text{cm}^2$  at wavelengths of 254, 365, and 185 nm, respectively. This lamp was controlled by a timer circuit which allowed programmable on/off cycling of power. The chamber could be baked at temperatures up to 473 K using external strip heaters, and the sample itself could be precisely controlled to levels above ambient (up to 773 K) by a pyrolytic boron nitride heater mounted inside the vacuum chamber.

### 2.2. Samples

Because the focus of this study is on ultraviolet radiation stimulated formation of iron oxides from oxyhydroxides at the Martian surface, lepidocrocite ( $\gamma\text{-FeOOH}$ ) and goethite ( $\alpha\text{-FeOOH}$ ) were the primary hydroxylated mineral phases that we studied. Anhydrous control samples included hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), and fused silica. All of the iron minerals used in our work were synthetic, commercial products with particle sizes of approximately  $0.5$   $\mu\text{m}$ . The hematite and goethite samples were manufactured by Pfizer, while the lepidocrocite and maghemite were obtained from ISK Magnetics. X-ray powder diffraction analyses were conducted to verify the composition and purity of the samples.

### 2.3. Procedure

In order to maximize the exposure of the mineral surfaces to ultraviolet radiation, while minimizing contributions to the overall uncertainty by grains not exposed to UV, a great deal of effort was expended to minimize the thickness of each sample while maximizing surface area. We suspended the submicrometer-sized mineral grains in water using ultrasonic agitation and subsequently "airbrushed" the mixtures using pressurized nitrogen onto the surfaces of 13 mm diameter fused silica disks. The disks were maintained at 383 K during deposition to remove the water before large droplets could form.



**Figure 2.** Raw mass spectrometer data from atomic mass unit 18 measured from lepidocrocite ( $\gamma$ -FeOOH) which was baked for 24 hours at 373 K. The ultraviolet lamp was cycled on/off (1 hour each) while these data were collected. Similar results were obtained for goethite ( $\alpha$ -FeOOH).

The total quantity of sample on each resulting disk was approximately  $10^{-4}$  g.

When the prepared sample disks were introduced, the upper portion of the vacuum chamber, which is separated from the ion sputtering pump by a gate valve, was opened in a glove bag under a positive-pressure flow of high-purity nitrogen. Once the chamber was resealed using a new copper gasket, sorption pumps immersed in liquid nitrogen were used to rough the upper chamber. At a pressure of 1 to 2  $\mu$ m as determined by a thermocouple gauge, the vac-sorbs were isolated, and the gate valve to the ion pump was reopened to resume an ultrahigh vacuum (UHV) chamber. The chamber walls and the sample were baked at  $\sim$ 423 and 373 K, respectively, for 24 hours to minimize the quantity of water in the system and in the sample. After baking, on/off cycles of the UV lamp (2 hour period) were initiated while the gas phase species in the chamber were monitored with the quadrupole mass spectrometer. Typical monitoring durations were approximately 150 hours with measurements collected every 20 s.

#### 2.4. Results

Figure 2 illustrates a raw data profile for the water vapor (AMU 18) in the chamber as a function of time as a lepidocrocite ( $\gamma$ -FeOOH) sample was periodically radiated with an ultraviolet lamp. Once the data were filtered to reduce instrumental noise and the DC bias was removed, the remaining AC signal (see Figure 3) could be analyzed for frequency content corresponding to the cycles of the UV lamp. The application of a fast-Fourier transform (FFT) to the data clearly shows that the power in the

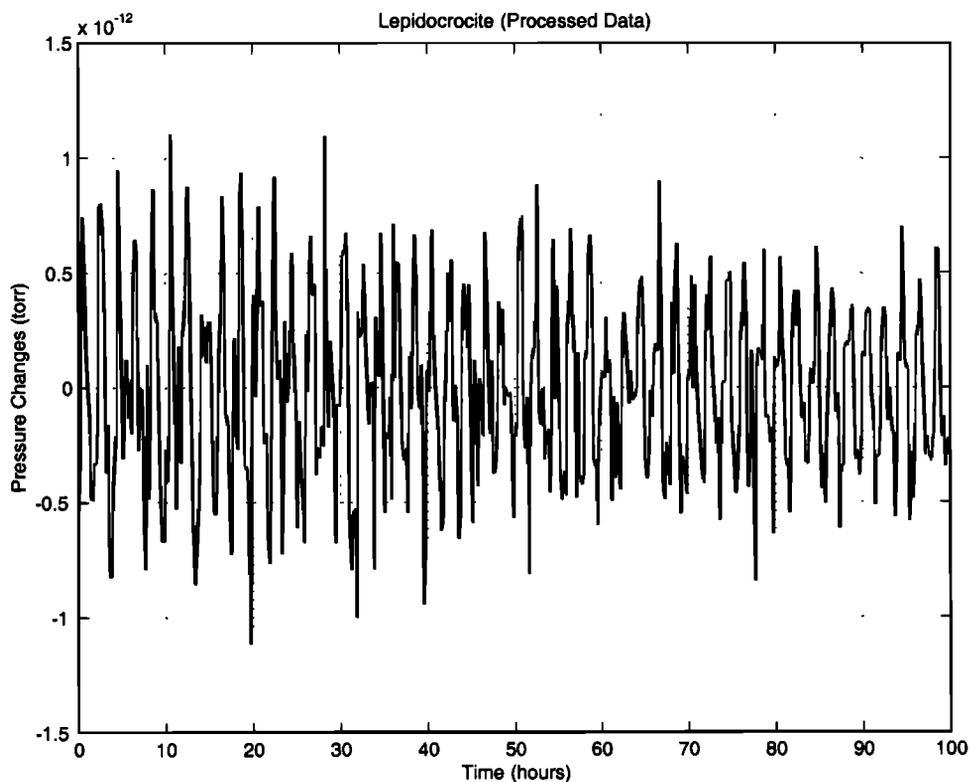
signal corresponds to a 2 hour period (Figure 4). Similar results were obtained for goethite. Thus the release of water from FeOOH in these experiments was correlated to stimulation from the ultraviolet lamp.

### 3. Interpretation

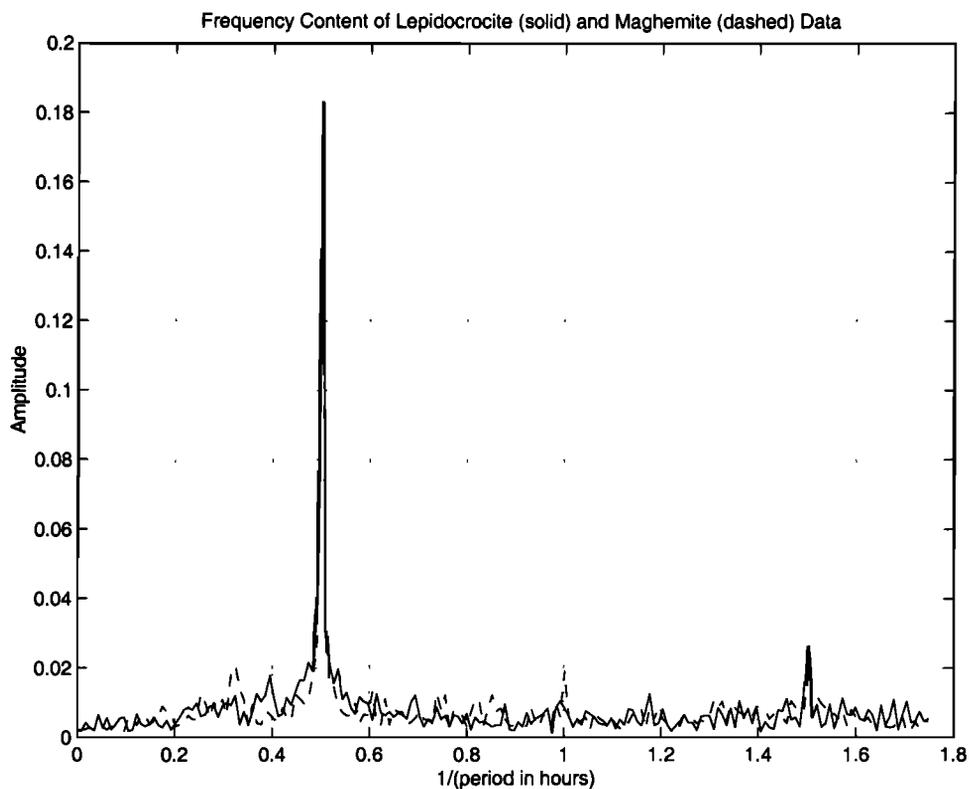
#### 3.1. Source of the Observed Water

Possible sources of the water molecules released by the ultraviolet lamp are as follows: (1) Adsorbed and trapped  $H_2O$  molecules on the samples, (2) OH on the grain surfaces (released as  $H_2O$ ), (3) the vacuum chamber itself, and (4) OH from the crystal structure of the samples (released as  $H_2O$ ). As discussed in the paragraphs below, we believe that the observed signal is most likely a result of ultraviolet-stimulated release of  $H_2O$  and possibly OH from the surfaces of mineral grains.

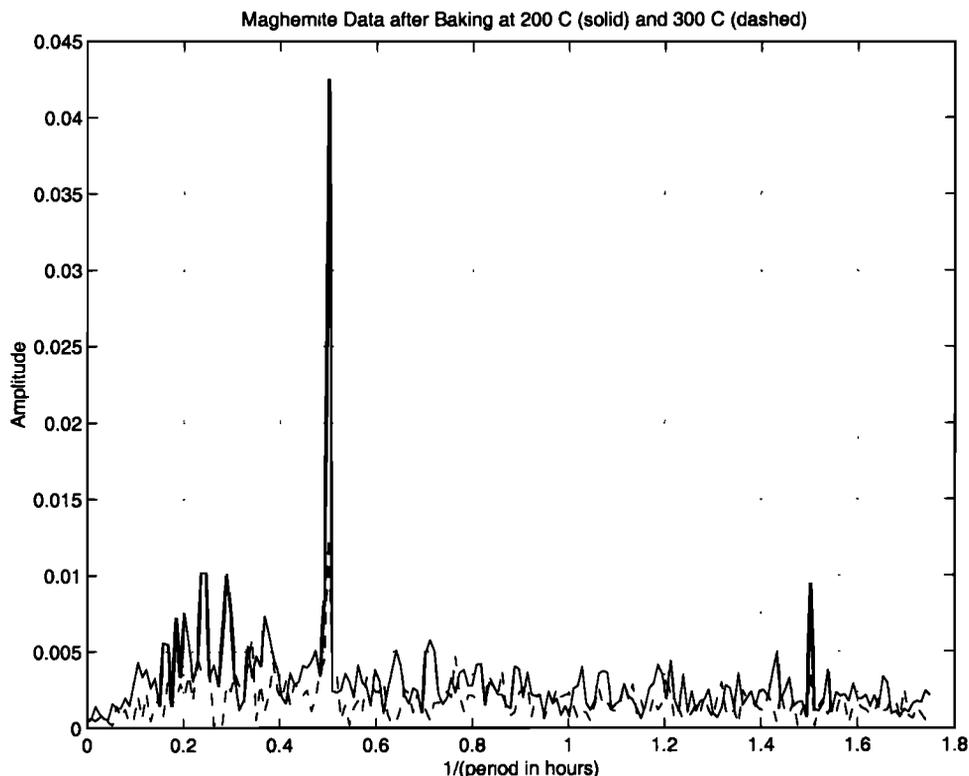
**3.1.1. Molecular water.** The intent of this study was to determine the rate of removal of structural OH from the crystal lattice, and trapped or adsorbed water on the samples resulting from exposure to laboratory air prior to chamber introduction was considered a noise source. Thus we baked each of our samples for approximately 24 hours at 373 K inside the vacuum chamber with ambient pressures between  $10^{-8}$  and  $10^{-10}$  torr. Studies of adsorbed water on crystal faces of metal oxides indicate that molecular water is not retained on surfaces under ultrahigh vacuum conditions at temperatures above approximately 275 K [Henderson, 1996]. However,  $H_2O$  molecules can remain trapped in pores, in fissures, and in the matricies of the mineral grains even after heating to temperatures much higher than our



**Figure 3.** Low-pass filtered version of the signal shown in Figure 2 with the trend removed.



**Figure 4.** Fast Fourier transform (FFT) of the data in Figure 3 (lepidocrocite, solid line) and for a similar data set collected for maghemite (dashed line). Each curve is an average of 400 separate 4096 point FFTs. The spike at a period of 2 hours corresponds to water released from the samples while the lamp was on. The lack of a significant difference between the results from lepidocrocite and maghemite indicates that trapped water or surface OH which remained on the samples was the source of the water signal.

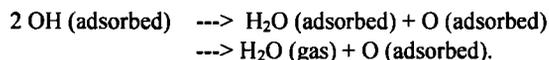


**Figure 5.** FFTs of the signals obtained from maghemite samples during exposures to cyclic UV radiation and after baking at 473 K (large peak) and 573 K (smaller, dashed peak) for 24 hours.

nominal bakeout [Thiel and Madey, 1987]. In our experiments, heating the samples to 473 and 573 K prior to exposure to the lamp reduced the evolved water signal by approximately 75% and over 90%, respectively (see Figure 5). We believe that bakeout to these higher temperatures thermally ejects more of the trapped water and decreases the quantity available for UV-stimulated release. We believe that trapped H<sub>2</sub>O is at least partially responsible for the experimental results.

**3.1.2. Surface OH.** The behavior of water molecules on surfaces of metals, semiconductors, and oxides has been extensively studied [e.g., Thiel and Madey, 1987]. Experiments with single-crystal hematite at room temperature show that water adsorbs dissociatively at steps and defects to form surface hydroxyl groups [Henrich and Cox, 1994; Kurtz and Henrich, 1987]. Powdered iron oxides, likely because of an abundance of facet edges, are very efficient at dissociating water and can result in as much as a monolayer of OH species on the surface [Knozinger, 1976]. These surface hydroxyl groups can be stable on samples at temperatures above our nominal bakeout [Thiel and Madey, 1987] and thus are likely to be present in our laboratory experiments.

As studied by thermal desorption and electron energy loss spectroscopy, a hydroxylated surface can release molecular water through the following pathway [Thiel and Madey, 1987]:

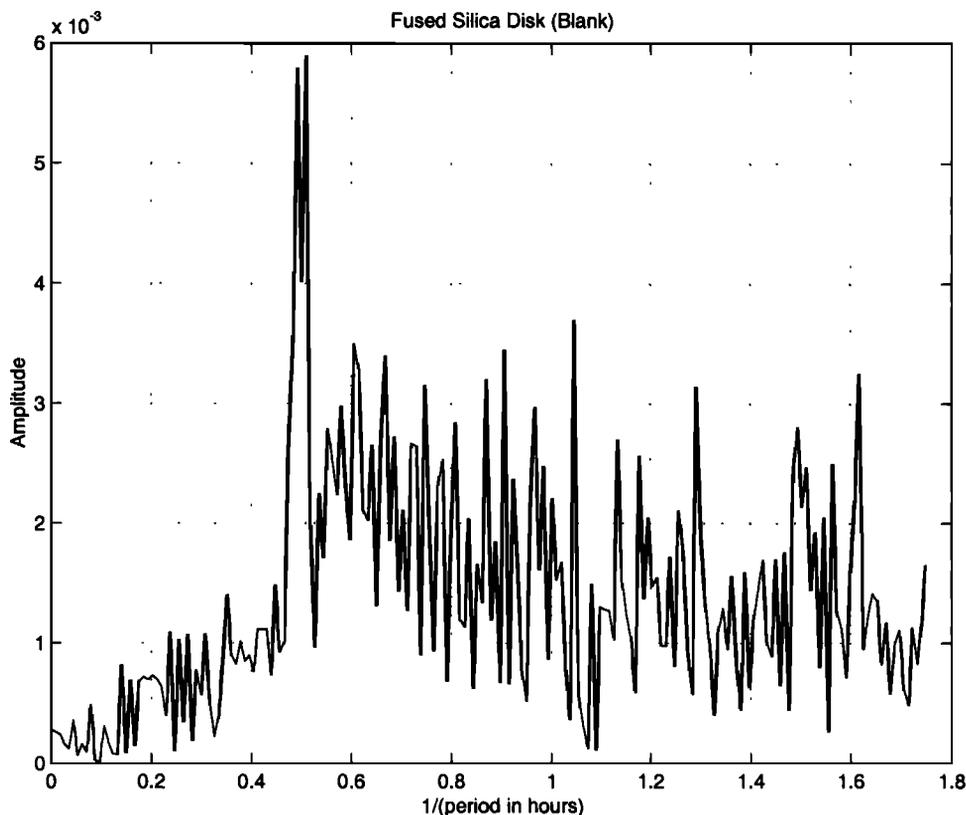


A photon stimulated, as opposed to thermal, mechanism for the release of water vapor from surface hydroxyl groups is described by Zhu *et al.* [1991]. In these UV laser (6.4 eV) experiments,

surface hydroxyl photodissociates to yield hydrogen in an excited state which subsequently combines with another surface OH to release water vapor. This process could also be occurring in our experiments; that is, the recombination of surface hydroxyl groups by photon stimulation could be contributing to the observed enhancement in water vapor during exposure to ultraviolet radiation.

**3.1.3. Vacuum chamber.** We investigated the possibility that interactions between the ultraviolet photons and the mass spectrometer or the vacuum chamber walls could be the source of an erroneous mass 18 signal correlated to the UV lamp. There have been reports of enhanced ionization efficiency by the Dycor head when exposed to UV photons (D. Athey, personal communication, AMETEK Corporation, Pittsburgh, Pa., July 1997). The construction of the chamber and sample fixture, however, does not allow direct illumination of the mass spectrometer. The only escape path for UV photons to the lower portions of the chamber is through openings designed for gases evolved from the sample, but all photons exiting by this pathway will first have interacted with the mineral grains, the fused silica sample substrate, or the boron nitride heater surface. Reflections from these surfaces will severely attenuate the ultraviolet photon flux in the lower chamber, where the quadrupole head is located. This configuration also serves to minimize the chamber surface area exposed to the ultraviolet photons. The top of the sample fixture is approximately 1 cm from the bottom of the Al<sub>2</sub>O<sub>3</sub> window, and the recessed sample platform is only 5 mm deep.

Stainless steel vacuum chambers, such as the one used in this experiment, will release water under ultra-high vacuum conditions through the recombination of OH, O, and/or H from the chamber walls [Thiel and Madey, 1987]. We confirm that the



**Figure 6.** FFT result from a blank fused silica disk exposed to cyclic stimulation from the ultraviolet lamp (2 hour period). Compare to Figures 4 and 5 and note that the signal is substantially weaker without the powdered ferric minerals. These results indicate that the water vapor pressure increase resulting from UV illumination of the chamber alone is insignificant relative to the water ejected from the mineral samples.

contamination from the vacuum chamber was minimal by using a blank fused silica disk as the sample. All other experimental procedures were identical to the cases where coated disks were introduced to the chamber. The FFT results while using this blank are shown in Figure 6. The magnitude of this response was approximately 30 times smaller than the nominal cases. Thus we conclude that UV interactions with the instrumentation or the vacuum chamber does not provide a significant contribution to the observed signal.

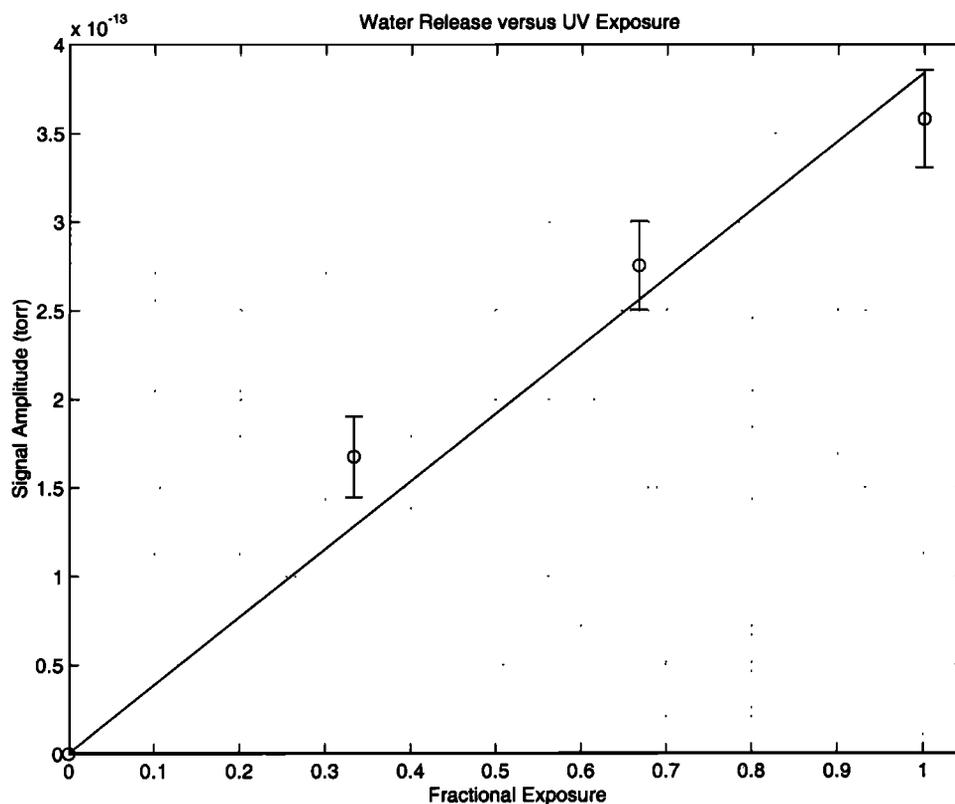
**3.1.4. OH from the crystal structure.** Lepidocrocite and goethite each contain hydrogen bound to oxygen in the octahedra of the crystal structure. Could the observed enhancement in water vapor concentration while the ultraviolet source was energized result from ejection of OH and H from these sites? To answer this question, we compare the results from the two phases of FeOOH to the results obtained from their oxide counterparts: maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). The process used in the preparation, baking, and data collection from the FeOOH polymorphs was carefully repeated for the  $\text{Fe}_2\text{O}_3$  samples. An FFT result for the gamma oxide phase is plotted in comparison to the oxyhydroxide in Figure 4. These spectra indicate that there is no significant difference between the amount of water released from lepidocrocite as compared to maghemite. Similar results were obtained for the other polymorph:  $\alpha\text{-FeOOH}$  (goethite) and  $\alpha\text{-Fe}_2\text{O}_3$  (hematite). Because maghemite and hematite do not have hydroxyl crystal unit cell, the enhancement in water vapor concentration observed during illumination cannot be from structural OH. Thus the

nearly identical results for both FeOOH and  $\text{Fe}_2\text{O}_3$  suggest that some source of water other than from the OH in the crystal structure was responsible for the signal observed for all of these ferric minerals. As described in the sections above, we believe that trapped  $\text{H}_2\text{O}$  and possibly surface OH were the sources of water in our experiments.

### 3.2. Mechanism

The process through which water is ejected from the samples could involve thermal effects or electronic excitation of the substrate, adsorbate, or adsorbate-substrate complex. As discussed in the following sections, we believe that a quantum process is the most likely.

**3.2.1. Thermal effects.** Is it possible that the evolution of water from our samples was due to thermal effects of the incident energy? The measured body temperature of the lamp was 368 K. Could this elevated temperature radiatively heat the sample, chamber walls, or the gas molecules and be responsible for the observed signal? There is, in fact, a history of misinterpretation of thermal effects: *Morris and Lauer* [1981] attributed the earlier report of photodehydration by *Andersen and Huguenin* [1977] to heating by unfiltered visible and near-IR radiation. As described in the following paragraphs, we attempt to minimize thermal effects by prebaking the samples and using a line source. Furthermore, we believe that equilibrium heating is not likely to be a significant factor in the release of water by showing that the yield is roughly proportional to the incident flux of ultraviolet photons.



**Figure 7.** Standard deviations of the time-varying signals plotted against the incident photon flux. Error bars were obtained from averaging over different time windows in the 100+ hour data sets. The roughly linear relationship implies that equilibrium heating was not responsible for the enhancement in water vapor concentration when the ultraviolet lamp was illuminated.

**3.2.1.1. Sample bakeout:** To minimize the contribution from visible and infrared photons in our experiments, we use a mercury vapor line source with a peak power output at 254 nm and a bulb temperature of only 368 K. This source is in contrast with high-pressure arc lamps that release most of their energy at visible and infrared wavelengths and have bulb temperatures well in excess of the levels necessary to thermally dehydroxylate our samples. Because of the low bulb temperatures in our experiments, we can easily prebake the samples to levels higher than achievable by radiative heating from the lamp. In fact, bakeout levels roughly double and triple the bulb temperature (473 and 573 K for 24 hours prior to UV illumination) continue to yield water vapor while the lamp was on (see Figure 5). Exposing the sample to these high temperatures, as well as the nominal bakeout level of 373 K, under vacuum should have released all of the water thermally accessible by a 368 K lamp. Thus we believe that the enhanced water vapor concentration in the chamber when the lamp was powered was not a result of thermal stimulation.

**3.2.1.2. Rehydration after bakeout?:** There is the remote possibility, however, that the sample surface can rehydrate from exposure to the background water vapor in the chamber (approximately  $10^{-11}$  torr) after the bakeout and rerelease water when exposed to the 368 K ultraviolet lamp. To ensure that such an indirect thermal process was not the cause of the observed signal, we varied the photon intensity using filters external to the chamber. The filters were designed to block 33% and 67% of the ultraviolet photons incident on the sample while maintaining

relatively uniform sample illumination (no direct shadowing). If a photon-stimulated process was responsible for the water release, as we believe, then the yield should be proportional to the number of photons hitting the sample per unit time. Figure 7 shows the amplitude of the time-varying component of the water vapor pressure does, in fact, vary linearly with photon intensity indicating that equilibrium heating of the substrate was not a factor in our experiments. Local heating effects are not completely ruled out by this plot because pseudo zero-order desorption kinetics could still result in a linear profile. However, we believe that the most likely interpretation of preheated samples yielding water vapor in proportion to incident flux is that thermal effects do not contribute significantly to the release of water vapor.

**3.2.1.3. Other thermal processes:** Low-energy electrons mobilized in the substrate by interactions with the ultraviolet photons can couple to the lattice and excite phonon modes [Zhou *et al.*, 1991]. This thermal process, while initiated by photons, can result in the desorption of the adsorbate if the binding energy is exceeded. Such multiple photon events, if present, would further enhance the rate of water ejection from the laboratory sample relative to an equivalent sample on Mars. Thus the minimum exposure times on Mars for dehydroxylation of a FeOOH sample (discussed in section 4) would be even greater than the calculated lower limit if this indirect thermal process were active in our experiments.

Another possibility is that sample heating is driving thermal recombination of surface hydroxyl groups to release water. This

process can occur at temperatures as low as 325 K [Henderson *et al.*, 1998], and our sample temperature of up to 310 K when the lamp was on is close to this value. However, prebaking the sample to 373 K should release the OH accessible by lamp heating. Furthermore, if rehydroxylation from the background water vapor in the  $10^{-11}$  torr chamber occurs after bakeout, one would expect similar results from preheating to 373, 473, and 573 K. As shown in Figures 4 and 5, this is clearly not the case, and we do not believe that thermal recombination of OH is a significant factor in our experiments.

**3.2.2. Electronic processes.** Unlike infrared energy which couples directly to the vibrational modes in the irradiated materials, ultraviolet photons interact electronically. Bond-breaking chemistry resulting from absorption of an UV photon can result from excitation of the adsorbate, the substrate, and the adsorbate-substrate complex. These photon-stimulated processes can result in desorption through the following pathways, as reviewed by Franchy [1998] and Zhou *et al.* [1991]: (1) Direct excitation of the adsorbate can be followed by desorption if the electronic transition from the ground state moves the adsorbate beyond the threshold distance necessary for escape. (2) Excitation of the substrate generates electron-hole pairs which migrate through the lattice and attach to the adsorbate, stimulating its release. (3) Other, more complicated, electronic excitations of the adsorbate-substrate complex resulting in desorption are also possible [Burns *et al.*, 1990]. The typical procedure for distinguishing between these various electronic pathways, as well as thermal processes such as equilibrium, local, or resonant surface heating, is to measure the velocity distribution of the desorbates as a function of wavelength and photon flux. However, because the primary purpose of this work is to establish constraints on the rate of dehydroxylation of mineral on Mars, we did not pursue identification of the specific mechanism of water desorption.

Our result which shows nearly identical responses for FeOOH and Fe<sub>2</sub>O<sub>3</sub> samples indicates that structural OH is not liberated by ultraviolet radiation. This clearly illustrates that energy alone does not determine whether atoms and molecules can be released from the crystal structure. A 190 nm photon incident on the Martian surface or a suspended dust particle has an energy of 6.5 eV, while the 254 nm photons used in our experiments correspond to 4.9 eV. O-H and Fe-O bonds have strengths of approximately 4.5 and 4.1 eV, respectively. The energy of the photons is sufficient to break the bonds, but the results presented here suggest that localization of the energy does not occur and the structural OH remains intact.

## 4. Application to Mars

The inability to dehydroxylate minerals, as shown in these laboratory experiments, has implications for the survivability of aqueous weathering products on Mars. Furthermore, ultraviolet-stimulated ejection of H<sub>2</sub>O or OH from grain surfaces could add a small source term to models of diurnal water cycles. "Order of magnitude" calculations are presented in the following paragraphs.

### 4.1. Structural OH

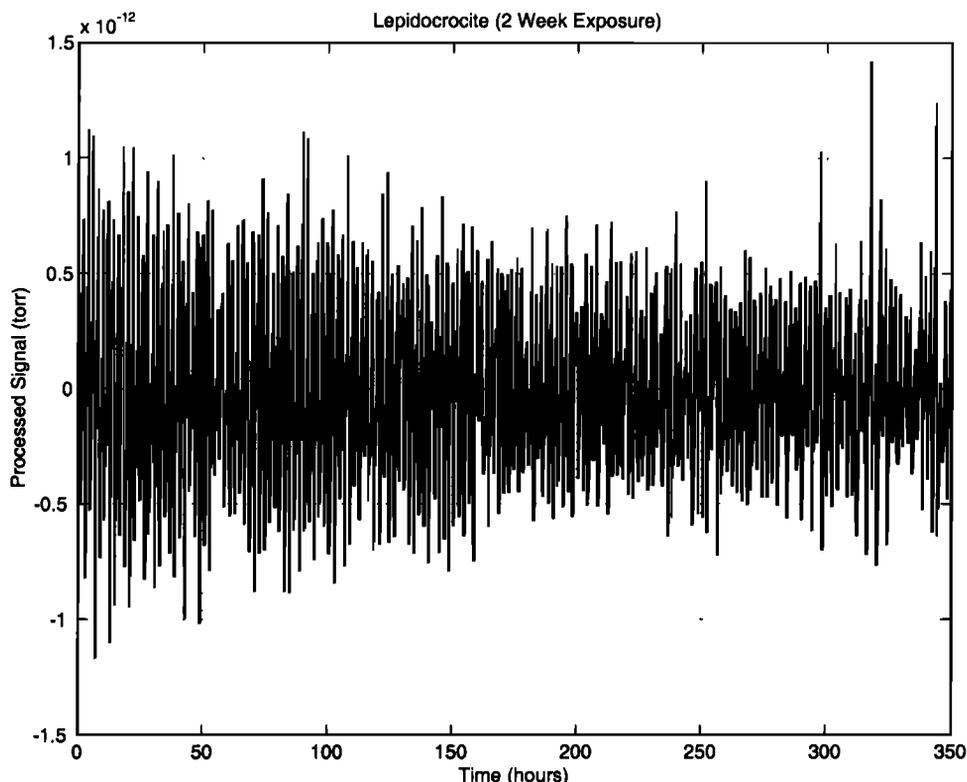
The current state of desiccation of the Martian soil [Yen *et al.*, 1998] and weakness [Murchie *et al.*, 1993] or absence [Dalton and Clark, 1995; McCord *et al.*, 1982] of the cation-OH vibrational mode of phyllosilicates (~2.2  $\mu\text{m}$ ) in reflectance

spectra are in apparent conflict with models of liquid water weathering of surface rocks [e.g., Burns, 1993]. Unless a mechanism for destroying hydroxylated minerals under Martian conditions is identified, the absence of these phases implies a relatively limited aqueous weathering history at the Martian surface. According to experiments and calculations by Pollack *et al.* [1970], dehydroxylation of FeOOH in the low water vapor pressure Martian atmosphere is kinetically inhibited even over timescales of  $10^9$  years. The process of converting FeOOH to Fe<sub>2</sub>O<sub>3</sub> by exposure to UV, if active, would imply that Mars could have had a past climate supportive of aqueous weathering at the surface, but no mineralogical evidence of that history at the surface today. Furthermore, if dust particles suspended in the atmosphere are more susceptible to dehydroxylation because of a larger UV dose, settling of these ubiquitous particles onto the surface could bias spectral observations. That is, radiation-altered dust may mask underlying materials of mineralogical significance. In our experiments, however, we obtain no evidence for photoinduced ejection of structural OH. This finding is in contrast with the results published by Mukhin *et al.* [1996], who found that carbonates and sulfates could be decomposed by incident UV. The efficiency of photodecomposition is apparently greater for carbonates and sulfates as compared to iron oxyhydroxides. On the basis of our experiments, we can set constraints on the rate of removal of water from iron oxyhydroxides.

**4.1.1. Surface soil.** The 10<sup>-4</sup> g FeOOH samples that were used in these experiments contain roughly  $10^{17}$  molecules of evolvable water from structural sites (~10% H<sub>2</sub>O by mass). We observe no measurable differences, for exposures of up to 250 hours of UV, between the quantity of water evolved from the oxyhydroxide as compared to the oxide samples used in the experiments and have attributed the observed signal to desorption of surface species. We estimate that the methods used here would allow us to detect UV stimulated dehydroxylation from lattice sites (i.e., differences between results from FeOOH as compared to Fe<sub>2</sub>O<sub>3</sub>) at rates as low as  $10^9$  molecules per hour. This sensitivity limit implies that UV photons could, in fact, be stimulating the release of structural OH at rates too low to be observable. Using these values for measurable release rates and total structural OH, samples could dehydroxylate in our laboratory experiments in timescales of  $10^4$  years or greater.

On Mars, geologic timescales are available, and  $10^4$  years is a geologically short period of time. However, the UV flux on Mars is substantially lower than in these laboratory experiments, resulting in an effective timescale for desiccation even longer than this  $10^4$  year lower limit. The samples in these experiments were exposed to roughly 5 mW of radiation at a wavelength of 254 nm (4.9 eV). Assuming all photons from 200 through 350 nm are capable of dehydroxylating Martian dust and sand grains at some very low rate, a comparison of the incident power can be made. An integral of Kuhn and Atreya's [1979] model for solar radiation incident on the Martian surface yields an approximate average flux of  $10^{-5}$  W cm<sup>-2</sup>. Thus these laboratory experiments provide a 500-fold enhancement of the ultraviolet flux as compared to the surface of Mars. Extrapolating to Mars using these energy ratios, an equivalent sample on the Martian surface would take  $>5 \times 10^6$  years to completely dehydroxylate. This extrapolation assumes that the pressure and temperature effects are not significant, which of course, is not completely true.

The  $\sim 10^{-10}$  torr vacuum and room temperature environment for the lab experiments will shift the mineral into the stability regime of the desiccated phase [Pollack *et al.*, 1970] and enhance



**Figure 8.** Extended duration exposure of a lepidocrocite sample to ultraviolet radiation cycles. The relatively small change in the amplitude over time is consistent with our estimate that complete removal of the adsorbed water would take  $\sim 10$  years in the laboratory configuration.

the rates of dehydroxylation relative to an equivalent sample on Mars. The low pressure in the experiment, however, is not as large of a factor as intuition would suggest. *Pollack et al.* [1970] quoted a  $1/e$  goethite dehydroxylation timescale of 67 hours for a temperature of 498 K under air. This value is consistent with the observation that heating a sample to 473 K for 24 hours under UHV conditions does not visibly convert the goethite to hematite. The interpretation is that the atoms inside the structure are not sensitive to the water vapor pressure at the surface of the grains and that the pressure regime experienced by the laboratory samples does not significantly influence the calculation of necessary exposure timescales on Mars.

Temperature, on the other hand, is a significant factor. For each  $10^\circ$  increase in temperature, the rate of dehydroxylation changes by a factor of 3 to 50, depending upon the activation energy of the process which ranges between 87.9 and 247 kJ/mol [Cornell and Schwertmann, 1996]. The temperatures which should be compared are the maximum surface temperature for Mars ( $\sim 280$  K) and the maximum sample temperature while the lamp is on ( $\sim 310$  K). This  $30^\circ$  difference corresponds to a factor of 40 to  $10^4$  change in the rates of dehydroxylation for the above activation energies. That is, if the minimum timescale for desiccation of a goethite or lepidocrocite grain is  $\sim 5 \times 10^6$  years on Mars (as extrapolated from a 310 K experiment), then the colder Martian temperatures would change this estimate to a range of  $10^8$  to  $10^{10}$  years. Given that the upper meter of surface materials is likely to be active at the present time [Christensen and Moore, 1992], the exposure time for a given soil/dust grain to ultraviolet radiation is likely to be much shorter than the 100 million year minimum exposure time for desiccation.

Furthermore, the effect of the ultraviolet radiation will only be on the immediate surface (upper few nanometers) of each grain. Diffusion of hydrogen to the surface sites accessible to the ultraviolet photons will further increase the necessary exposure time for grain dehydroxylation.

Based on an extrapolation of our laboratory results to Martian conditions, we conclude that ultraviolet radiation-induced removal of OH from the structure of hydroxylated iron phases such as goethite and lepidocrocite is not a geologically significant process on Mars. The result implies that the ferric oxides at the Martian surface did not form by UV-stimulated dehydroxylation of FeOOH. Thus the present mineralogy of the Martian surface layer is not necessarily an indication, as many have suggested, that Mars had a rich history of aqueous weathering.

**4.1.2. Suspended dust.** The minimum timescale for the ultraviolet radiation-induced dehydroxylation of Martian dust particles could be a factor of 10 shorter than the 100 million year minimum calculated above. Periodic storms continually inject small particles into the Martian atmosphere, where they experience a larger UV flux (due to the shorter atmospheric path length) than mineral grains at the surface. This  $10^7$  year timescale is a minimum value set by the sensitivity limits of our experiments. The actual required exposure time could be much longer and possibly irrelevant to the weathering processes on Mars.

#### 4.2. Desorption of Water From Soil Surfaces

In an "order of magnitude" estimate, the background pressure of water vapor in the chamber corresponds to  $5 \times 10^{10}$  molecules, and the application of the UV source raises the pressure by a few

percent while the ion pump continues to operate. Using an estimate of the volume of the chamber and the pumping rate for water, we calculate that  $8 \times 10^9$  molecules of water were released from the sample each hour during exposure to the UV photons. Assuming that each mineral grain retains the equivalent of 0.1 monolayer of water as trapped molecules or surface hydroxyl and using a measured BET surface area of  $18 \text{ m}^2/\text{g}$ , each sample exposed to UV radiation in our experiment would contain approximately  $10^{15}$  molecules of ejectable water. If this quantity of water were accessible and permanently ejectable by photostimulation, it would take more than 10 years to accomplish. Thus our laboratory experiments cannot realistically carry the surface dehydration to completion. This calculation is consistent with the relatively constant water signal during extended exposures (Figure 8). If it takes 10 years to remove the trapped water and surface OH from a sample in the vacuum chamber, it would take  $\sim 5 \times 10^3$  years for the same process to occur on Mars (using the energy scalings described above). This rough calculation does not account for the initial quantity of water on the Martian soil grains nor the diurnal cycles of UV radiation flux.

In the actual Martian environment, we expect the soil particles at the immediate surface and the suspended dust particles to equilibrate with the surrounding atmospheric water vapor. In the daytime, however, temperature and pressure are not the only factors that need to be considered to determine the quantity of water present. Our experiments show that ultraviolet radiation-induced desorption of water is important as well. The rates of evolution of water calculated above are applicable to the initial quantities of water and OH in the laboratory samples which are retained under an ultrahigh vacuum environment at 373 K and greater. A similar calculation using surface area estimates for the Martian soil ( $75 \text{ m}^2/\text{g}$ ) and estimated quantities of adsorbed water ( $\sim 5 \times 10^{-5}$  g of  $\text{H}_2\text{O}$  per square meter of soil surface area) by Zent and Quinn [1997] suggest that in a 10 hour exposure to ultraviolet radiation, a square meter of the Martian surface could evolve up to a milligram of water from UV stimulation alone. Thus UV radiation could add a small source term to the models of diurnal water cycles [Jakosky et al., 1997; Zent et al., 1993].

## 5. Conclusions

1. Our experiments show no evidence that ultraviolet radiation is capable of liberating OH from the lattice structure of hydroxylated mineral phases. Based on the sensitivity limits of our experiments, we calculate a minimum required UV exposure time of  $10^8$  years for photodehydroxylation of lepidocrocite or goethite at the Martian surface. Because the actual value could be much higher and because the timescale of overturning for surface materials is likely to be shorter than this  $10^8$  year minimum, we conclude that UV radiation-induced removal of structural OH from minerals is not a significant process at the Martian surface.

2. The applicability of photodehydroxylation to Martian dust particles is enhanced relative to soils at the surface. Suspension in the atmosphere, periodic dust storms, small particle sizes, and the greater UV flux at higher altitudes all increase the possibility that ultraviolet radiation can induce the removal of structural OH from hydroxylated phases in the Martian dust. While the sensitivity limits of our experiments set a shorter minimum exposure time for dehydroxylation of suspended dust as compared to surface minerals ( $10^7$  versus  $10^8$  years), the actual

required time could be much longer, and we still have no evidence to support the occurrence of this physical process.

3. The inability to identify an ultraviolet radiation-stimulated process for destroying hydroxylated minerals over geologic timescales on Mars implies that such phases formed at the surface during the suspected water-rich climatic episodes in the past may still be there today. The lack of clear evidence for such minerals at the Martian surface suggests that the aqueous weathering environment may have been relatively limited.

4. Laboratory experiments show that ultraviolet radiation incident upon samples of lepidocrocite, maghemite, goethite, and hematite is capable of releasing trapped water and/or surface hydroxyl in the form of water vapor. An extrapolation to Martian conditions suggests that up to 1 mg of water could be released per square meter of the surface during daytime exposures to ultraviolet radiation.

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