

ULTRAVIOLET RADIATION-INDUCED DEHYDRATION OF MINERALS: NEW EXPERIMENTS. A.S. Yen¹, B.C. Murray¹, F.J. Grunthaler², and G.R. Rossman¹, ¹California Institute of Technology, Division of Geological and Planetary Sciences, 170-25, Pasadena, California 91125 (ayen@earth1.gps.caltech.edu), ²Jet Propulsion Laboratory, MicroDevices Laboratory, 302-306, Pasadena, California 91109.

Chemical weathering models and morphologic data suggest that abundant hydrated minerals are formed on the surface of Mars. Viking Lander *in situ* measurements, however, evolved less than 2 weight percent water from samples heated to 500°C. New experiments show that thin films of goethite can be dehydrated by exposure to ultraviolet radiation flux, thus affording one possible mechanism for dehydration.

Observations and models of the Martian surface environment indicate that primary basaltic rocks and volcanic glasses have been altered to secondary mineral phases. Many of these chemical weathering products are believed to be hydrated. Based on geologic scenarios, thermodynamic calculations, and infrared spectroscopy, much published literature infers the presence of palagonites on the surface (Soderblom and Wenner, 1978; Gooding and Keil, 1978; Allen, 1979, 1980, 1981; Singer, 1982; Morris et al., 1990). Other work contends that smectite clays dominate the Martian fine particles (Baird et al., 1977; Clark et al., 1982; Zolotov et al., 1983; Zolensky et al., 1987; Banin et al., 1985, 1988). Burns, 1988, indicated that spectral data are consistent with ferrihydrite, jarosite, opal, and clay silicates. The presence of iron oxhydroxides also has been suggested (Morris et al., 1983; Banin et al., 1985; Singer, 1985). Based on Mariner 6/7 infrared reflectance data, Calvin et al., 1994, set an upper limit of 10% to 20% for the presence of hydrous carbonates. Thus, these mineralogical descriptions of the Martian surface suggest an abundance of hydrated phases.

In contrast, Houck et al., 1973, obtained 3 micron spectra of Mars, and on theoretical grounds, they estimated the scattering coefficients for the surface and constrained the water content of the soil to be approximately 1% by weight. The only direct measurement of the water content of the Martian surface materials was performed by the gas chromatograph - mass spectrometer (GC-MS) instrument onboard the Viking Landers. Also in contrast to the implications of the chemical weathering models, remote sensing data, and geologic formation scenarios, the GC-MS results from one of the landers indicate that approximately 2% water by weight was evolved from each of two samples heated in rapid (30 second) steps to 500°C (Biemann et al., 1977).

We are attempting to show experimentally that the Viking data and remote sensing spectra are consistent in terms of water content. Fourier transform infrared

(FTIR) reflectance spectra are being obtained from plausible mixtures of Mars-analog minerals. Differential scanning calorimetry and thermal gravimetry are being used to quantify the water content of the samples. Preliminary results suggest that even small amounts of hydrous minerals can easily (but not uniquely) produce absorption spectra qualitatively similar to the ISM spectra. Thus, we infer that Mars' soil is probably quite dehydrated by terrestrial standards. Evolved water predictions for the Mars '98 Surveyor lander thermal and evolved gas analyzer (TEGA) will be presented at the meeting.

Exposure to the Martian environment over geologic time scales could have removed the initial water content of the hydrated minerals modeled to be present. On thermodynamic grounds, however, Pollack et al., 1970, concluded that there would be little net loss of goethite over the life of Mars. Ultraviolet radiation induced dehydration was suggested by Andersen and Huguenin, 1977. According to their abstract, photons with wavelengths shorter than 280 nm release H₂O (g) from goethite by ejecting OH⁻ ligands which subsequently combine with H⁺ from nearby sites. Morris and Lauer, 1981, however, repeated the experiments and found no UV dehydration effects on goethite (a-FeOOH) or lepidocrocite (g-FeOOH) in exposures equivalent to 10 to 100 years on the Martian surface.

Our second set of new experiments utilize a quadrupole mass spectrometer to measure the evolution of water as a function of temperature for thin films of goethite. Thin layers are used to maximize the surface area to bulk mass ratio to increase the probability of measuring a surface process (upper few hundred nanometers). This iron oxide polymorph was selected to allow direct comparisons with previous work. Synthetic a-FeOOH grains with an average dimension of 250 nanometers are suspended in water using ultrasonic agitation. The mixture is subsequently "airbrushed" onto the surface of 0.5 inch diameter fused silica disks using high-purity nitrogen. The disks are heated to 110°C during deposition to remove the water before large droplets form. The total quantity of goethite on each disk is approximately 20 micrograms.

These samples are placed into an ultra high vacuum (UHV) chamber evacuated to 10⁻⁸ torr using an ion pump. One sample is exposed to 254 nm radiation from a mercury vapor lamp through a sapphire window

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while the other sample is held as a control. The samples are then heated to 500°C, and the evolved water (mass 18) is measured as a function of temperature. Figure 1 illustrates the results from two samples, one which is exposed to UV for 200 hours (lower curve) and the control. Results thus far indicate that ultraviolet radiation is capable of enhancing the rate of dehydration of goethite in high vacuum conditions, but more confirmation is required.

Two types of tests are ongoing to establish that the samples compared in the experiment are nearly identical: (1) The coatings on the disks are dissolved in HCl, diluted with HNO₃, and analyzed for ⁵⁷Fe content using an Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). In this instrument the acidic solution is metered at a known rate, atomized in an argon plasma, and quantified using a quadrupole mass spectrometer. (2) Goethite coated disks are linearly heated to 500°C and the evolution of water from two disks is compared. Initial results indicate that the variations in iron and water content of the initial samples are small compared to the difference between the two curves shown in figure 1.

We believe that our technique has several orders of magnitude greater sensitivity than previous experimental methods. Initial results suggest the presence of a UV dehydration effect observable in laboratory timescales. The dehydration of goethite and possibly clay minerals to simpler oxides could reconcile the weathering models with the Viking Lander GC-MS data.

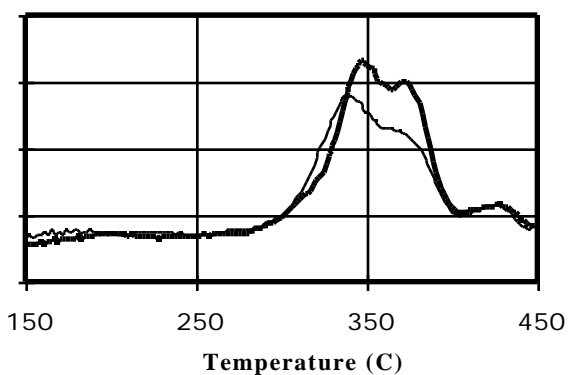


Figure 1: Water released from goethite as a function of temperature. Upper curve (at 350°C): No UV exposure; lower curve: ~200 hours of exposure to mercury vapor lamp.

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