THERMAL AND EVOLVED GAS ANALYSES OF SMECTITES: THE SEARCH FOR WATER ON MARS.

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Introduction: The theme of NASA's Mars Exploration Program is to "follow the water." Water has important implications in the search for life, climate evolution, evolution of the Martian surface and interior, and preparing for human exploration. The two Viking Landers detected small amounts of water (e.g., 1-2 wt. %) in the surface materials [1]. However, it is not known how the water is incorporated into these materials. From Viking data, it appears that most of the water evolved between 350 and 500°C. It was difficult to interpret the water data in terms of mineralogy because of the uncertainty of the Viking GC-MS measurements; the large temperature increases between evolved gas analysis (150°C) precluded obtaining an accurate temperature for evolution of water, and there are a large number of candidate minerals that may evolve water in this temperature range. Water evolved between 350 and 500˚C indicates that the water is structurally bound. A variety of minerals may evolve water in this region, including phyllosilicates, iron oxyhydroxides, some sulfates (e.g., Fe and Al sulfates), and hydrated glass (e.g., palagonites, hydrated amorphous Si).

Weathered basaltic materials near the summit of Mauna Kea Volcano on the Island of Hawaii are spectral and magnetic analogues for the ferric-rich materials that dominate bright Martian surface regions. We are using AVIRIS (Airborne Visible Infrared Imaging Spectrometer) remote sensing observations to both map the spatial distribution of the alteration products and to simulate observations that are planed by the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) instrument as a part of the 2005 Mars Reconnaissance Orbiter payload. AVIRIS is a hyperspectral imaging instrument that covers the wavelength range from about 0.4 to 2.5 µm. AVIRIS data (taken from about 20 km altitude) for Mauna Kea suggest three spectrally distinct hematite units, three phyllosilicate units (i.e., montmorillonite, saponite, and kaolinite units), a palagonite unit, and scattered jarosite units [2].

In this paper, we have chosen one of the phyllosilicate AVIRIS units (montmorillonite) as a test case to use thermal and evolved gas analyses (TA/EGA) to ground truth the spectral data. The AVIRIS montmorillonite unit also appeared to have signatures for nontronite, i.e., Fe-OH adsorption features. We show here that TA/EGA techniques have the potential to distinguish various smectite end members, i.e., montmorillonite from nontronite.

TA/EGA has the potential to be a powerful method to identify and characterize the volatile-bearing phases in Mars surface materials [e.g., 3,4]. The Thermal Evolved Gas Analyzer (TEGA) was designed to characterize the volatile-bearing phases on Mars [5]. TEGA consists of a differential scanning calorimeter integrated with a mass spectrometer. The 2007 Mars Phoenix Scout Mission will have an enhanced version of TEGA as part of the payload.

Materials and Methods: A smectite-rich sample (HWMK269) from the Puu Poliahu cinder cone near the summit of Mauna Kea Volcano in Hawaii was chosen as a test case for TA/EGA. The mineralogy of HWMK269 is dominated by plagioclase feldspar and smectite with minor amounts of magnetite and trace hematite. Laboratory spectra for VNIR and SWIR regions suggest that the smectite is predominately montmorillonite; however, weak Fe-OH and Mg-OH bands might indicate nontronite and saponite, respectively. Two distinct smectite end members (montmorillonite, nontronite) were chosen for TA/EGA to compare to HWMK269. Smectites are from the Clay Minerals Society reference clays repository: nontronite API-33; montmorillonite STx-1. A Perkin Elmer DSC-7 differential scanning calorimetry (DSC) was modified to conduct variable-pressure thermal analysis [3]. Platinum ovens were used to heat samples at a temperature ramp rate of 20°C/min with a Ar or N_2 carrier gas at 760 and 100 torr pressure. Only the 100 torr pressure results will be presented here; 100 torr represents the operating pressure used by TEGA.

Results and Discussion: The thermal analysis (TA) of most smectites is characterized by two distinct regions of water release. Water driven off before 300˚C is adsorbed water and hydration water of exchangeable cations. Water released between 300 to 700˚C is due to dehydroxylation of structural water. TA/EGA can be used to distinguish between the various smectites [6], although the distinction is complicated by the presences of other water-bearing phases (e.g., 1:1 phyllosilicates, hydrated glass or Si, Fe-oxyhydroxides, other 2:1 phyllosilicates, etc.). Water release curves at 100 torr pressure are shown for the smectites in Figs. 1 and 2.

We have previously shown that the appearance of curves for 100 and 760 torr are similar; however, onset temperatures for water release under 100 torr conditions are about 35˚C lower for water release events and sometimes, the water release curves are slightly narrower, i.e., narrower temperature range [3,7]. Water release curves for nontronite show that dehydroxylation onset occurs around 250˚C and has a peak around 400˚C (Fig. 1). This peak is very broad and may represent either dehydroxylation of a combination of Fe-OH and Al-OH from different octahedral coordination sites and/or contamination from other water-bearing phases (e.g.,. Fe-oxyhydroxides). The water releases peaks around 100˚C represent the release of adsorbed water and water associated with interlayer cations. Montmorillonite had an onset dehydroxylation temperature around 525˚C and peaks around 650-675˚C (Fig. 2). This dehydroxylation event primarily represents the thermal break down of Al-OH (and possible some Mg-OH) in the octahedral layer.

The TA/EGA curves for HWMK269 are shown in Fig. 3. The water curve has a very distinct and well defined curve for the release of adsorbed water and water associated with interlayer cations, which suggests a smectite phase. HWMK269 has a broad dehydroxylation event with an onset temperature around 320˚C with a peak around 575˚C. The peak temperature for this event suggests that the water release is best represented by Al-OH dehydroxylation for montmorillonite. AVIRIS spectra data and laboratory IR spectra for HWMK269 also suggest mainly montmorillonite and possibly nontronite.

The use of TA/EGA for mineralogical characterization is not straightforward and can be greatly complicated by a number of factors. For example, kaolinite also has a dehydroxylation event around 525˚C, but might be distinguished from smectite by the lack of a well defined water release peak for interlayer water. The presences of other smectites, e.g., saponite, will also complicate the interpretation of TA/EGA; hence, this method becomes most powerful when used with other techniques. For example, AVIRIS and laboratory VNIR/SWIR spectral data showed a broad Al-OH band near 2.2 µm, which suggested the presences of montmorillonite in HWMK269. We have also conducted XRD analysis on various particle sizes of HWMK269 and confirmed only the presences of a di-octahedral smectite.

Implications for Mars: The TA/EGA behaviors of Mars analog materials, such as HWMK269, will provide needed characterization of water-bearing and other volatile-bearing phases that might be encountered on Mars during robotic missions. CRISM on MRO will search for secondary alteration phases such as smectite. TEGA onboard the 2007 Mars Scout Mission will provide the opportunity to “ground truth” the CRISM results by constraining the mineralogy of bound water phases as well as provide fundamental understanding of water processes on Mars.

References: [1] Biemann K. et al. (1977) *J. Geophys. Res.* 82, 4641-4658. [2] Guinness et al. (2002) *LPSC XXXIII*, Abst. #2007. [3] Lauer Jr. H. V. et al. (2000). *LPSC XXXI*, Abst. #1990, (CD-ROM). [4] Ming et al. (2003) *LPSC XXXIV*, Abst #1880. [5] Boynton et al. (2001) *JGR-Planets* 106, Num. E8, 17,497-17,698. [6] Borchardt G. (1989) In *Minerals in Soil Environments*, SSSA, Madison, WI. [7] Golden D. C. et al. (1999) *LPSC XXX*, Abst. # 2027 (CD-ROM).

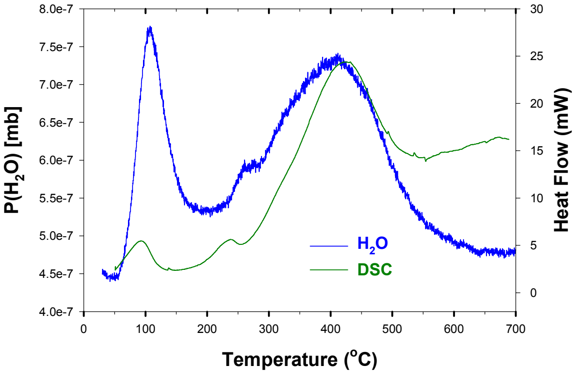

FIGURE 1 : DSC and water release curves for nontronite (100 torr N_2 carrier gas at 20 sccm).

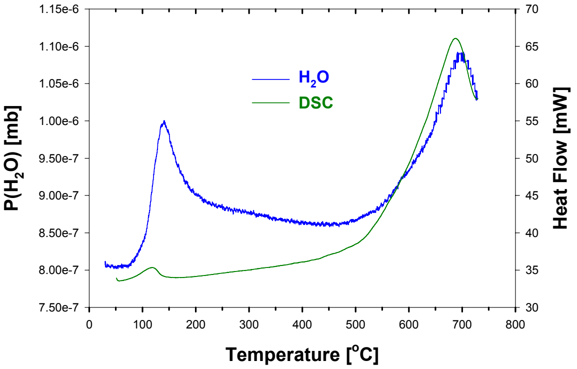

FIGURE 2: DSC and water release curves for a montmorillonite (100 torr N_2 carrier gas at 20 sccm).

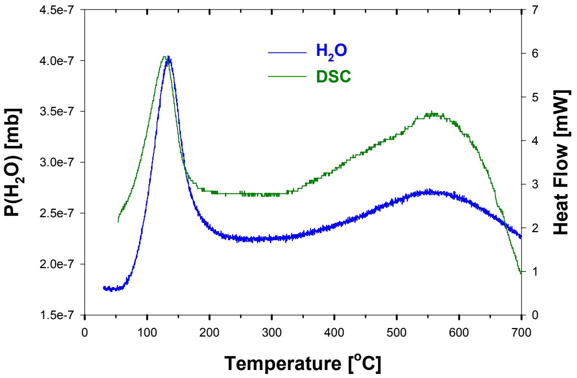

FIGURE 3: DSC and evolved water curves for Mars analog sample HWMK269 (100 torr Ar carrier gas at 20 sccm)