MID-IR FIBER OPTIC PROBE FOR IN SITU WATER DETECTION AND CHARACTERIZATION.

I. Garrick-Bethell[1], M. A. Thomson[2], and P. J. Melling[2], [1]MIT Department of Aeronautics and Astronautics, Cambridge, MA, iang@mit.edu, [2]Remspec Corporation, Sturbridge, MA, mat@remspec.com.

Introduction: Mid-IR fiber optic probes offer a flexible sampling geometry with access to the important spectral range between 2 and 10 microns. Spectra of soils and rocks at these wavelengths offer a wealth of information about the presence of water and other volatiles. Other fiber optic probes for near-IR and Raman spectroscopy are under development [1,2], but their sensitivity to some important species is lower than what can be attained with the mid-IR. For example, the near-IR region (typically up to 2.5 microns) samples overtones of water vibrations, and does not capture the stronger fundamental modes that appear in the mid-IR. In Raman systems the selection rules are different, and polar bond vibrations such as O-H and N-H do not appear strongly in the spectrum. Using the greater sensitivity of the mid-IR spectral range, hydrated minerals, adsorbed water, and very low amounts of water ice can be detected and characterized. The mid-IR probe used in this study is made from chalcogenide glass optical fiber, which is the most technically mature type of mid-IR fiber, and fully covers the fundamental O-H stretch region where other solid mid-IR fibers do not [3]. It has low mass, uses minimal power, operates under low temperatures, and can be coupled to most FTIR spectrometers. In order to characterize the instrument's performance in detecting low levels of water and OH, spectra of 6 samples were collected.

Sample selection: Samples were chosen to represent possible targets on other worlds. The first sample is a portion of dried streambed sand, meant to emulate physical properties of regolith. The second is solid CO_2 (dry ice) with a small coating of frozen water, meant to simulate possible volatile mixtures present on the poles of Mars. The third sample is from the clear and colorless rim of a grossular garnet from Lake Jaco, Mexico, chosen to test the instrument's ability to detect low levels of incorporated OH. Previous mid-IR studies of grossular near the 3600 cm^{-1} band have shown that structural $(OH)_4$ substitution for SiO_4 is typically below 0.3% by mass (expressed as percent mass of H_2O) [4]. The fourth sample is Y-type zeolite, which should contain more than a few percent of water by mass. The fifth sample is an impure olivine section of a Brahin stony-iron Pallasite meteorite. The last sample is ambient laboratory room air, chosen to determine water vapor detection capabilities.

Methods: The fiber optic reflectance probe was manufactured by Remspec Corporation (Sturbridge, MA), and the spectrometer was built by Bruker Optics Inc. (Billerica, MA). All spectra were sampled from 2-10 microns, for 5 minutes, with a wavelength resolution of 4 cm^{-1}. Spectra are obtained in absorbance mode by taking the ratio of the single-beam spectrum against an air background with the probe head approximately 2-3 mm above the sample. All samples except the dry ice were at room temperature, approximately 20° C. The lab air spectrum was collected in "double pass" transmittance mode by reflecting the signal from a polished aluminum surface approximately 5 mm from the probe head.

Results: All solid samples except the grossular contain a broad peak near 3300 cm^{-1}, Fig. 1. Notably, this feature in the dry ice sample contains a "grassy region" of mixed peaks, and a sharp double peak near 2360 and 2335 cm^{-1}. The atmospheric spectrum also contains grassy features in the bands near 3600 and 1600 cm^{-1}, along with the same double peak (dip) as the solid CO_2 sample, Fig. 2. The grossular sample contains a small bump near 3650 cm^{-1}, and a strong peak towards the end of the spectrum at 1060 cm^{-1}. Figure 3 shows a close up of the grossular feature near 3660 cm^{-1}, which consists of three peaks at approximately 3686, 3660, and 3632 cm^{-1}.

Features present at 2160 cm^{-1} in all spectra are due to imperfections in the fiber, but this contaminant can be easily avoided in the future.

Discussion: The locations of the three peaks in the grossular sample around 3660 cm^{-1} correspond closely to the spectrum of the OH region sampled from the colorless rim of a Lake Jaco grossular garnet in [4] (see Fig. 12). The Lake Jaco grossular in [4] contained 0.03% H_2O by mass. Since our sample is from the same geologic feature, has the same color properties, and is similar in spectral features, it is reasonable to assume that the probe can detect structurally incorporated water at the 0.03% level. A more conservative estimate is 0.1%. If a significant amount of adsorbed water were present it would be visible near 3400 cm^{-1}, so nearly all of the OH observed is structurally bound. This ability to distinguish between different types of OH vibrations (e.g. adsorbed, structurally incorporated, free water, etc.) is a powerful feature of the mid-IR spectrum compared to the near-IR.

The broad 3300 cm^{-1} features in the dry ice spectrum indicate water ice, and demonstrate the instrument's ability to detect and characterize water in macroscopic amounts. The "long grass" appearance of the region is attributable to spectral features arising from vapor-phase water over the sample, which exhibit rotational fine structure. The signal near 3300 cm^{-1} in the zeolite spectrum is particularly strong since zeolite is highly absorbent and has a high water content. The meteorite and sand also exhibit the 3300 cm^{-1} water feature. The probe's sensitivity to atmospheric water is visible in the stretch and bend features at 3400 and 1650 cm^{-1}, respectively, which exhibit characteristic splittings due to rotational coupling (Fig. 2). The sharp double peaks near 2360 cm^{-1} in both air and carbon dioxide spectra are due to C-O stretching modes in vapor-phase carbon dioxide.

Potential missions: The instrument's sensitivity to OH makes it particularly useful for detecting water in typically anhydrous environments. Two example mission targets are the purported deposits of water ice at the lunar poles, and hydrated minerals on carbonaceous asteroids [5]. The regolith on these targets is likely homogenized and can be sampled at colder (less noisy) temperatures, therefore detecting OH signals *in situ* should be as achievable as it is for grossular in the lab. Characterizing water at locations with significant water content, such as Mars's north pole, is also possible. Since the mid-IR spectrum gives information on CO_2 and OH, the instrument could characterize mixtures of regolith, water, and CO_2. When the probe is not taking spectra of solids on Mars, it could be aimed at a reflective surface a short distance away to measure fluctuations in local atmospheric water content.

Deployment scenarios: All possible deployment geometries have the advantage of bringing the probe head to the sample, avoiding disturbance of the sample and the need for sample processing hardware. For rock samples, a robotic arm could position the probe against the target. Insertion of the slender fiber and probe into a rock borehole could also be accomplished. Regolith spectra can be obtained either by directly placing the probe near the surface, or by pushing it below the surface by means of applied force or a digging device. The probe could also be deployed with a Raman fiber optic system to enhance the mission's rock identifying capabilities.

Instrument design: A complete mid-IR fiber optic package requires a mid-IR interferometer light source, spectrometer, fiber optic bundle probe, detector, and a Sterling cycle cooling unit for the detector head. Not including the spectrometer, all other components have a combined mass of less than 2 kg, and require less than 15 W of power. The probe used for this study has a lower temperature limitation below -196°C (absent rapid temperature cycling). The required spectrometer could be adapted from a Mars mission Michelson spectrometer already flown [6], and double as a thermal emission spectrometer. The estimated mass for the spectrometer is 2.4 kg.

Conclusion: A mid-IR fiber optic probe offers a spectral range appropriate for detecting and characterizing low amounts of OH with a flexible geometry that allows *in situ* measurements. Water detection below 0.1% (1 ppt) by mass can be expected.

References: [1] Stoker, C. R. et al. (2003) Sixth International Conference on Mars, LPI Contribution No. 1164, Abstract #3007. [2] Haskin, L. A. et al. (2003) LPS XXXIV, Abstract #1651. [3] Mizaikoff, B. (2003) *Analytical Chemistry, 75*, 258A-267A. [4] Rossman, G. R. and Aines, R. D. (1991) *American Mineralogist, 76*, 1153-1164. [5] Rivkin, A. S. et al. (2002) chapter in *Asteroids III*, U. Arizona Press, 235-253. [6] Christensen, P. R. et al. (2003) *JGR, 108*, 8064.

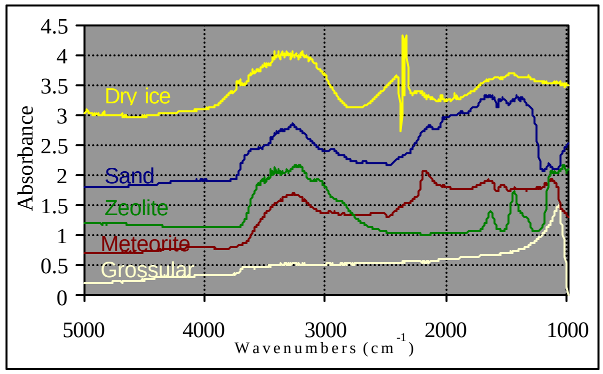

Figure 1. Spectra of the 5 solid samples.

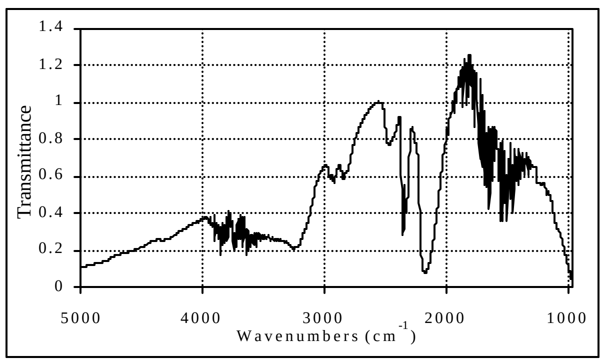

Figure 2. Atmospheric transmittance spectrum.

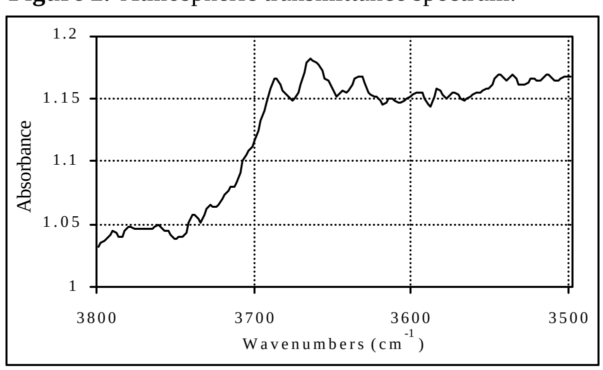

Figure 3. Close up of the grossular OH region.