

THE WATER-WHEEL IR (WIR) – A CONTACT SURVEY EXPERIMENT FOR WATER AND CARBONATES ON MARS. Alian Wang, Larry A. Haskin, John Freeman, Edward X. Dong, Karla E. Kuebler, Dept. of Earth & Planetary Sciences & McDonnell Center for Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130. (alianw@levee.wustl.edu).

Water and Carbonates on Mars: Minimum requirements for life include water and accessible carbon. Mars has both in its polar caps and atmosphere. Water (or water-equivalent hydrogen) is present at shallow depths (~10 – 20 cm) at latitudes $\geq 60^\circ$ and is heterogeneously distributed in other parts of Mars [1]. Mars may have once had surface water that could plausibly have produced carbonate deposits [2-5]. Mars shows signs of hydrothermal activity [6-8] that may have affected soil composition [9, 10]. The Thermal Emission Spectrometer on the Mars Global Surveyor found large and small patches of hematite that may have been water-borne or water-derived [11, 12]. Current orbiting spacecraft (MGS & Odyssey) have not found massive carbonate deposits, however [13]. Shales and limestones, which we associate with moist and benign environments on Earth, are apparently not abundant on Mars. Both carbonate and organic carbon occur as alteration products in Martian meteorites of igneous origin [14]. One study of MGS-TES data suggests 2-5 wt% carbonates (mainly MgCO_3) in surface dust, but found no concentrated source [15]. Carbonates and $\text{H}_2\text{O}/\text{OH}$ bearing minerals will be sought by the mini-TES and Mössbauer experiments on the Mars Exploration Rovers, one of which landed successfully on Mars on January 3.

WIR – a Contact-Survey Experiment: The water-wheel IR experiment is designed to detect directly water in different forms (liquid, ice, or clathrates, structural H_2O and OH, and water adsorbed on grain surfaces), carbonates, and under favorable conditions sulfates and C-H & N-H bonds in organic species.

WIR will use an *active near IR (2-6 μm) reflective spectrometer* installed inside a well set into the middle wheel of a planetary rover. During rover travel, when the well is at nadir, the IR sources will irradiate soil disturbed by the front or rear wheel of the rover. Radiation reflected from the sample (mainly diffuse reflection) in the 2-6 μm spectral range will be collected and recorded. The measurement will not interfere with the normal activity of the rover. Information on the spatial distribution of the above-mentioned phases will be obtained along the rover traverses. WIR is a *Contact-Survey* experiment. It will observe thousands small (~1 cm^2) patches of soil at near contact range. Examining a small area at a time enables observation of relatively sparse species that are concentrated in a given area, without the spectral background of major materials in a broader area in which the species is a minor or trace component. This

enhances the probability of finding rare substances.

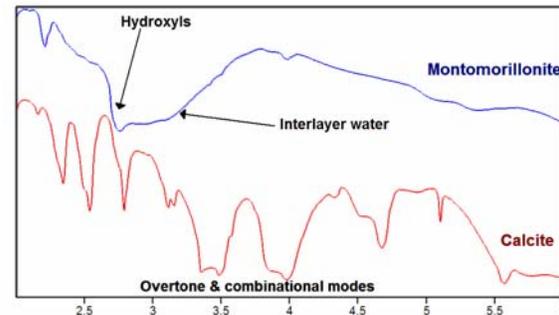


Figure 1 % Reflectance spectra of a clay and a carbonate in 2-6 μm range

Because solar radiation and thermal emission from surface materials do not provide adequate intensity for on-surface spectroscopy in the 2 - 6 μm region, WIR sensor will use active IR sources emitting in the desired spectral region with sufficient and stable intensity, an advantage for on-wheel deployment and close-up sensing. The 2-6 μm spectral range contains the strongest bands for the fundamental vibrations of free water, adsorbed water, structural H_2O and OH in minerals (2.7 – 3 μm), and those of C-H (3.1 – 3.5 μm) and N-H bonds (4.1-5.0 μm), so detection sensitivity is high (Fig. 1a). This range is also sensitive for observing carbonates through two strong overtone and combinational bands (~3.4 and ~3.9 μm , Fig.1b). Their characteristic band shapes and positions stand apart from the overtone and combinational bands of silicates, so carbonates can be detected in silicates at very low concentration. Sulfates have a combinational band occurs near 4.5 μm , which overlaps silicate bands of similar type. The 2-6 μm range also includes the bands (~2.2 -2.3 μm) frequently used by VIS/NIR spectroscopists for the detection of phyllosilicates and carbonates (Fig.1).

The WIR sensor uses reflectance geometry, an advantage for detecting IR bands in the 2 - 7.5 μm spectral range. Reflectance spectra in this range are dominated by volume scattering and absorption band troughs, such that most IR photons are absorbed in the band center and are scattered away at the band wings. Owing to the specific combinations of absorption coefficients, mean optical path length, and particle diameter, bands from fundamental O-H and C-H stretching vibrations and from overtone and combinational tones

of carbonates, sulfates, and some silicates in this spectral range are *disproportionally enhanced*. This offers a great advantage for detecting these phases at very low concentrations; 0.25 wt % calcite was detected in a quartz matrix of 0-75 μm size range in a laboratory [16].

Breadboard and Simulation: A proof-of-concept breadboard of the WIR was built in our laboratory, using four active near IR emitters, conical IR collecting optics, a commercial spectrograph, and a 256 pixel PbSe array detector. The testing and optimization of the breadboard are still underway.

Tests on detection limit and low spectral resolution were made on a laboratory IR spectrometer (ThermoNicolet Nexus 670) using a Harrick Cricket™ biconical reflectance unit. Samples of calcite [CaCO_3], talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], and gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] were separately pulverized and sieved to collect the 75-150 μm particle size range, which were hand mixed with either a fluorite [CaF_2] or a quartz [SiO_2] matrix of same size range. Mixtures from 0.1 mole% to 15 mole% were made, and the IR spectra were measured in triplicate on separate sample fillings of the IR sample tray. Both total reflectance (specular plus diffuse) and diffuse-only reflectance spectra were acquired.

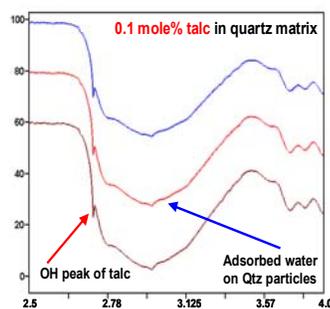


Figure 2 Triplicate % reflectance spectra of 0.1 mole % talc in quartz matrix

The OH peak of talc at 2.72 μm is detectable at the 0.1 mole% level in mixtures with fluorite and quartz (Fig. 2). The 3.4 and 3.9 μm carbonate bands are detectable at the 0.1 mole% level in calcite-fluorite mixtures and at the 0.3 mole% level in the calcite-quartz mixtures (consistent with [16]). The H_2O peak of gypsum is detectable at the 0.05 mole% level in fluorite or in quartz. The sulfate combinational band ($\sim 4.5 \mu\text{m}$) occurs near a similar band of silicates, so the visual detection of sulfates is only achievable at much higher concentrations. Based on these data, we anticipate that as little as 0.5 - 1 mole% carbonate and water would be detectable by the WIR sensor in a natural setting.

In the IR reflectance spectra of a powdered mixture, the IR band area in the Kubelka-Munk (KM) plot of the reflectance data is proportional to the volume concentration of the species. A semi-quantitative determination can be extracted from the IR band area ratio. Figure 3a shows the % reflectance spectra of

calcite-quartz mixture at different calcite concentrations and Figure 3b shows a linear correlation between the known calcite concentrations in quartz and measured KM band area ratios (3.4 μm band of calcite to 4.4 μm band of quartz). Triplicate data points of the same concentrations demonstrate the repeatability of the measurements. Factors affecting the precision are the heterogeneity of sample mixing, packing variations, and sample surface flatness. In a natural setting, the number of components and their respective differences in grain size would also affect the precision; we anticipate a rough quantification to be achievable.

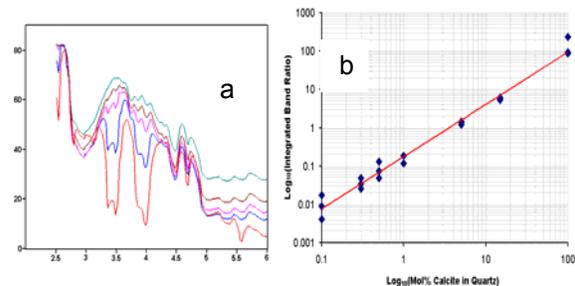


Figure 3 a) % Reflectance spectra of calcite-quartz mixtures and b) the correlation of KM band area ratio with concentration.

Water molecules from the terrestrial laboratory atmosphere are readily absorbed on the surfaces of fine grains in all these mixtures, which show broad water bands centered at $\sim 3 \mu\text{m}$ (Fig. 2 & 3a). On Mars, where the atmospheric water concentration is low, the WIR can detect adsorbed water on fine grain surface and its temporal variation as well as map variations in near-surface H_2O concentration.

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