ABUNDANCE AND ELECTRICAL PROPERTIES OF INTERFACIAL WATER IN THE MARTIAN REGOLITH. R. E. Grimm[1], D.E. Stillman[1], S.F. Dec[2]. [1]Dept. of Space Studies, Southwest Research Institute, 1050 Walnut St. #400, Boulder, CO 80302 (grimm@boulder.swri.edu; dstillman@boulder.swri.edu); [2]Dept. of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO (sdec@mines.edu).

Introduction. Interfacial water is present as thin, unfrozen films surrounding soil or rock surfaces at subfreezing temperatures [e.g., 1]. The intermolecular forces that form interfacial water result in adsorption, capillarity, frost heaving, and even freezer burn. On Mars, interfacial water may provide a medium for solute transport [2], attenuate electromagnetic signals [3], or even provide microbial habitats [4,5]. Our program to characterize interfacial water on Mars includes determination of unfrozen water content using nuclear magnetic resonance (NMR), measurement of broadband electrical properties, thermodynamic theory of interfacial water, and quantitative assessment of lithoautotrophic habitability.

Abundance. Our initial work focuses on the Mars-regolith analog JSC Mars-1 [6,7]. Distilled water was added to an oven-dried sample to obtain a mixture containing 33.4% H_2O by weight. A small portion (0.2 g) was used for the NMR measurement of temperature-dependent water content. The ^1H NMR spectra were recorded on a Chemagnetics Infinity 400 NMR spectrometer operating at 400 MHz for ^1H. Transverse relaxation times (T_2) were measured using the Carr-Purcell-Meiboom-Gill (CPMG; [e.g., 8]) pulse sequence using 90° and 180° transmitter pulse lengths of 5.5 μs and 11 μs, respectively, a delay of 40 μs between 180° pulses, and a delay of 1 s between each 180° pulse train. CPMG echoes were recorded using twenty different 180° pulse trains with 2 to 20 180° pulses with an increment of two 180° pulses; therefore the time τ at which the echoes were recorded were 0.08 to 1.60 ms with an increment of 0.08 ms. The observed integrated echo intensity from was corrected for ^1H background signals by subtracting the signal obtained from the empty sample cell for each τ-value. The corrected integrated echo intensities, $M(\tau)$, were fit to a function of the form

$$M(\tau) = \sum_n A_n(T)\exp(-\tau / T_{2n}) \qquad (1)$$

where $A_n(T)$ is the porosity of component n at temperature T and T_{2n} is the transverse relaxation time of component n. For JSC Mars-1 only one T_2 component was required to fit the $M(\tau)$ values for temperatures below freezing. Two T_2 values were required for the CPMG control experiment recorded at 6ºC. The amount of unfrozen water at any temperature is simply proportional to the ratio of the sum of the amplitude coefficients (here, a single value) to the sum of amplitude coefficients at the reference temperature (here, two values), multiplied by the known water amount at the reference temperature. These results may be compared to an empirical formula by Anderson and Tice [9] for terrestrial permafrost that predicts unfrozen water content solely as functions of temperature and specific surface area. We determined the specific surface area of JSC Mars-1 to be 85.1 m^2/g using nitrogen adsorption (note that this value is substantially larger than the Viking Lander measurement of 17 m^2/g [10]). The predicted abundance of unfrozen water agrees with observations to within ~20% over the measured temperature range (Fig. 1), but systematic variations are present. Specifically, the Anderson-Tice formula asymptotes at low temperature to an irreducible amount of unfrozen water, whereas our NMR measurements do not yet extend to sufficiently low temperatures to reveal this trend, if present.

Electrical Properties. Samples of JSC Mars-1 with 33.4% H_2O by weight were independently prepared for frequency- and temperature-dependent electrical-properties measurement. These samples are considerably larger than those used in the NMR. The sample holder was a three-electrode parallel-plate capacitor. This capacitor was then inserted into a heavily insulated freezer with a liquid nitrogen boost. A temperature controller maintained desired temperatures within ±0.5 K. Measurements were obtained with a Solartron 1296A Impedance Analyzer with a 1296A Dielectric Interface. Temperatures were decreased slowly to impede bubble and crack formation, and reconnaissance measurements made to ensure that the sample's electrical properties are not changing. Once stabilized, a detailed measurement was taken and the temperature is then slowly lowered to its next level, etc. The sequence was repeated with increasing temperature without observing any hysteresis, and repeat measurements were made to ensure reproducibility. Impedance measurements were converted to electrical properties using standard formulae.

Several features are evident in the electrical properties of Mars JSC-1 (Fig. 2). Prominent dispersion (e.g., slope steepening in the real dielectric constant) near ~10 kHz is the dielectric relaxation of ice [11]. Additional dispersion near 1 MHz is a dielectric relaxation associated with JSC Mars-1 itself [12]. The low-frequency asymptote in resistivity is taken to be the DC limit, ρ.

Electrical Mixing Model. The very high resistivity at low temperature indicates that, to first order, DC conductivity in Mars JSC-1 itself is negligible. This is unremarkable, as almost all DC conduction is either electrolytic or electronic, and there is no free metal in Mars JSC-1. We therefore chose to fit the DC resistivity simply as a function of the volume abundance of unfrozen water (i.e., an equivalent saturated porosity ϕ) and a fixed reference resistivity ρ_w taken to be that of the fluid at 23ºC. Numerous mixing laws exist [e.g., 13]; we found that a very shallow power law was necessary to fit the NMR observations (Fig. 1):

$$\phi = (\rho_w/\rho)^{1/6} \qquad (2)$$

with ρ_w = 3 Ω-m. The 6th-power dependence of resistivity on porosity is much stronger than commonly inferred for Archie's Law (2nd power) or the classic Looyenga model (3rd power). We interpret this as a manifestation of discontinuity in electrical connectivity with decreasing temperature.

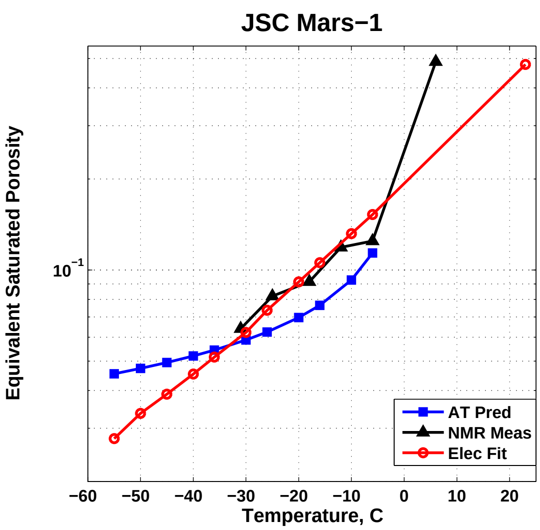

Figure 1. Interfacial water content predicted from empirical Anderson-Tice [9] formula (squares), measured by NMR (triangles), and fit from electrical properties (circles). Form of mixing law used to fit electrical properties implies increasing disruption of electrical connectivity at low frequency, beyond simple thinning of interfacial water.

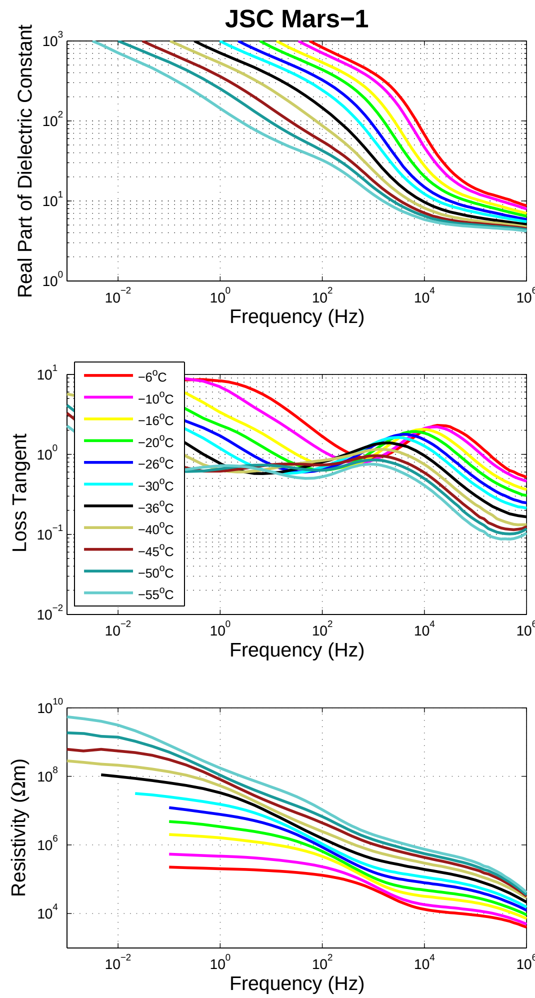

Figure 2. Electrical properties of Mars JSC-1 from –55ºC to 23ºC. See text for interpretation. DC conductivity used in Fig. 1 is the low-frequency asymptote of bottom panel.

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