

# **Charge Mobility in Ice Brines and Ice-Silicate Mixtures**

**Robert E. Grimm**

Department of Space Studies  
Southwest Research Institute  
1050 Walnut St. #300  
Boulder, CO 80302  
720-240-0149  
grimm@boulder.swri.edu

**David E. Stillman**

Department of Space Studies  
Southwest Research Institute

**Steven F. Dec**

Department of Chemistry and Geochemistry  
Colorado School of Mines  
Golden, CO

**Mark A. Bullock**

Department of Space Studies  
Southwest Research Institute

**John C. Prisco**

Department of Ecology  
Montana State University  
Bozeman, MT

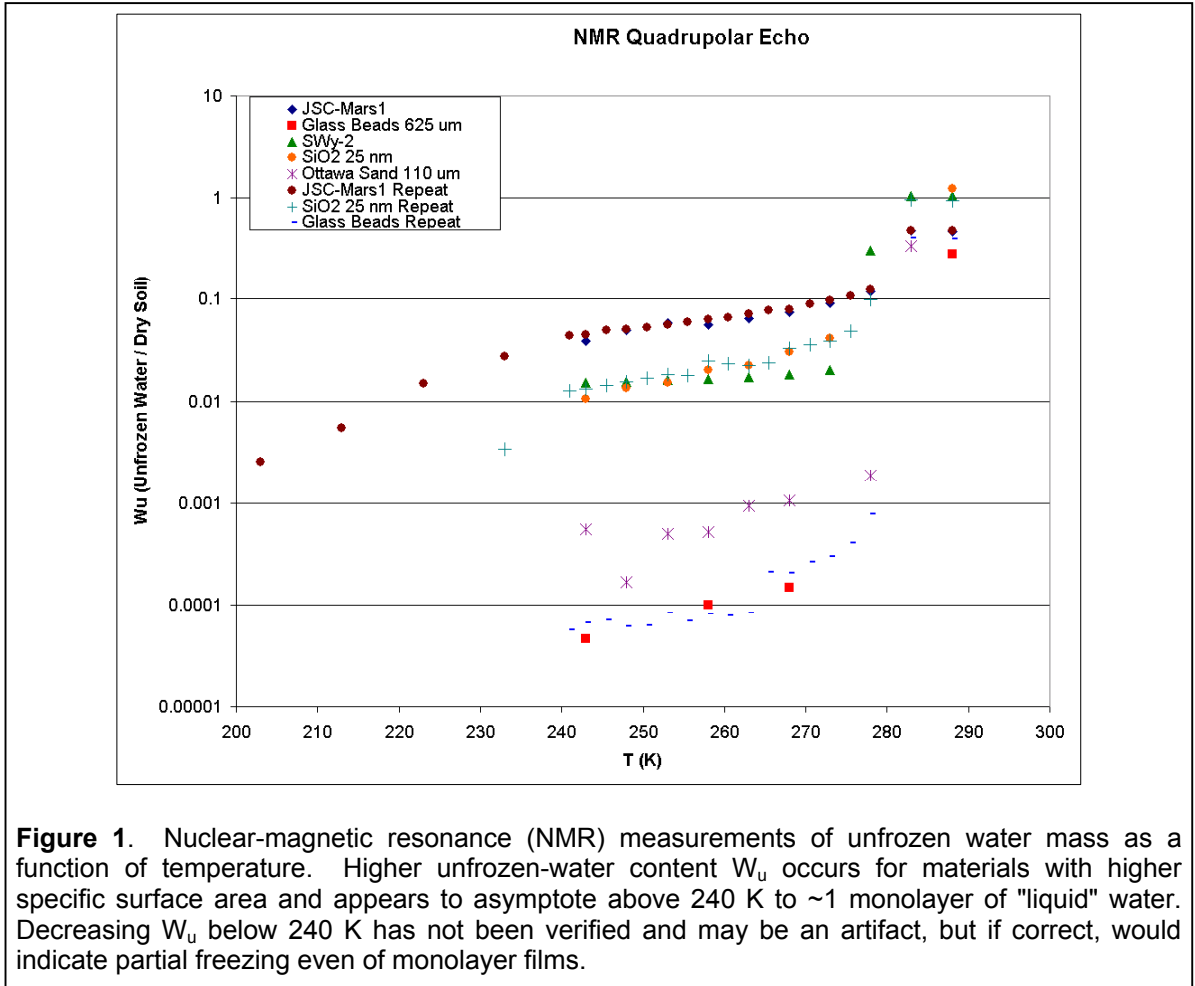
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Unfrozen water is present as thin films surrounding soil or rock surfaces at subfreezing temperatures. This water exists due to intermolecular forces between water and solids and is manifested as both capillarity and adsorption. It is distinct from supercooled water and from brine channels formed by impurity exclusion during ice freezing. Unfrozen water has been previously detected using nuclear magnetic resonance (NMR) down to the temperature of liquid nitrogen (77 K), whereas brine channels eventually freeze out at eutectic temperatures some tens of degrees below 0°C. Intermolecular unfrozen water has been hypothesized to provide habitats for microbial growth, on either a transient or permanent basis. This project quantitatively examines the exobiological viability of water thin films from both theoretical and experimental perspectives. For the former, we use model chemistries for Mars groundwater combined with fundamental thermodynamic considerations to identify favorable lithoautotrophic redox reactions and their limits in resource-limited environments. For the latter, we use NMR to measure the unfrozen water content of Mars analog materials to temperatures down to -90°C and compare these measurements with theory. Measurements of electrical conductivity reveal the efficiency of ion transport necessary to support microbial life and also provide the link to electromagnetic observables at Mars. In our previous report we described co-investigator problems with regard to the electrical measurements that slowed the start of the project: these were resolved by setting up our own lab under internal funding and by adding Dr. David Stillman to the team.

While assembling and testing the new lab last year, we focused on the theoretical potential for life in water thin films. Dr. Steve Jepsen and Dr. John Priscu, co-investigators at Montana State University, developed a computer model of the fundamental mass and energy balance of lithoautotrophic microbes. Dr. Mark Bullock provided data on inorganic water chemistries that may be appropriate to the shallow subsurface of Mars. From this starting chemistry, Dr. Jepsen's model identified  $\text{Fe}^{2+}$  as the most efficient electron donor and  $\text{NO}_3^-$  or  $\text{O}_2$  as optimum terminal electron acceptors. In the closed-system model, biomass production was limited by  $\text{Fe}^{2+}$  and metabolically required P. Dr. Grimm analyzed limits to biomass in shallow thin films of water imposed by locally available nutrients and/or aqueous advection or diffusion. The work, recently published in *Astrobiology* (Vol. 7, Nr. 2, pp. 342-354, 2007), confirms that such environments are harsh, with instantaneous biomass comparable to or less than those found in extreme environments on Earth. Furthermore, most microbes are forced into long periods of maintenance or survival modes. Our laboratory measurements, described next, impose even stricter constraints on life in interfacial water.

We performed numerous NMR experiments in the past year to quantify the unfrozen water content ( $W_u$ ) in host (solid) / ice mixtures (e.g., **Figure 1**). Ultimately, Dr. Steve Dec (co-investigator at the Colorado School of Mines) found that deuterated ("heavy") water produced the most robust NMR signal from the small sample size that could be accommodated in the 400-MHz spectrometer. This requires an analytical correction to  $W_u(T)$  due to the differences in melting point and latent heat (not shown in Fig. 1) but yields very robust results.  $W_u$  increases with specific surface area (SSA,  $\text{m}^2/\text{g}$ ) of the host material and asymptotes to a value corresponding approximately to one monolayer of "liquid" water coating grain surfaces.

NMR detection of unfrozen water in a variety of materials at temperatures more than several tens of degrees below freezing confirms long-held concepts about the persistence of liquid properties at very low temperatures. It is not the whole story, however. Our calculation of monolayer water thicknesses—reasonably consistent over nearly two orders of magnitude in specific surface area—calls into question the ability of these very thin films to act as solvents and

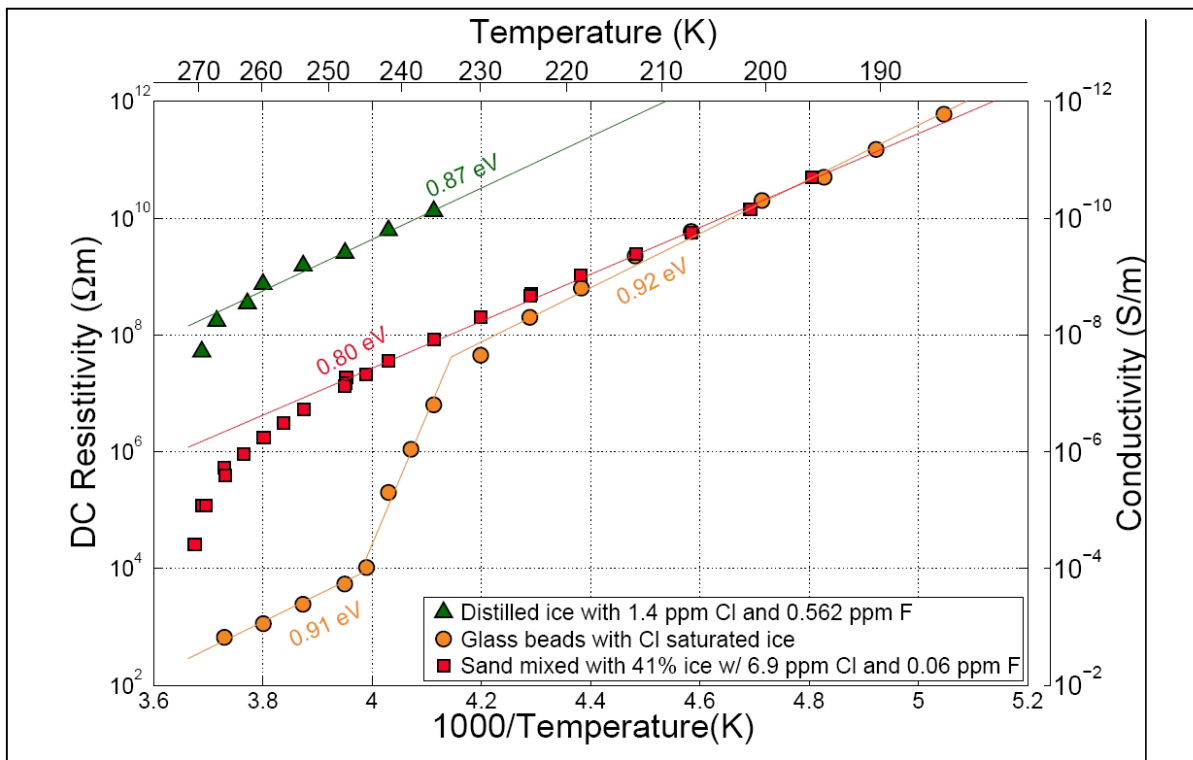


thus provide ionic dissociation and transport necessary to nutrient supply and waste disposal for metabolic activity.

Electrical conductivity provides the necessary test of ionic transport, because electrical conductivity in earth materials is dominantly electrolytic. Nonelectrolyzed liquid water itself is insulating; it is ions in solution that engender conduction under modest electric fields. The intrinsic conductivity of silicates is also small. The electrical conductivity of ice—logarithmically intermediate between electrolytic solutions and anhydrous silicates—is due to protonic point defects in the solid H<sub>2</sub>O structure.

Our measurements of the conductivity of ices and silicate-ice mixtures (**Fig. 2**) suggest a common temperature dependence (activation energy) at low temperatures, which implies that the conductivity there is dominated by the ice. In other words, low-temperature monolayer films, if preserved, cannot conduct electrolytically. Therefore unfrozen water at many tens of degrees below freezing—Mars ambient temperatures—cannot support ionic transport necessary for microbial metabolism. A corollary is that radar attenuation should not be affected by the DC conductivity of unfrozen water at these temperatures. These results are supported by other conductivity measurements that are not shown here for brevity.

Within ~30°C of melting, however, conductivities depart from a uniform activation energy to anomalously high values. These higher conductivities are likely due to some combination of



**Figure 2.** Electrical resistivity (and its reciprocal, conductivity) of water ice and sample solids saturated with ice. Anomalously low resistivities above 240 K are either due to liquid water, either as molecular-force thin films or brine channels formed from excluded impurities during freezing. Near-constant activation energy at lower temperatures indicates a common conduction mechanism, probably protonic point defects. These results suggest that the conductivity of water thin films below a few tens of degrees below freezing is negligible, and therefore thin films cannot support microbial activity at present temperatures near the surface of Mars.

unfrozen interfacial water and freezing-point depression in brine channels formed from exclusion of impurities from the freezing ice. These higher temperatures are within the range of terrestrial permafrosts, well-documented psychrophilic microbial activity, and may apply to higher obliquity states of Mars in different epochs.

With these working hypotheses in hand, our Year 3 work will focus on more systematic characterization of the conductivity and unfrozen-water content of ice-silicate mixtures as functions of ice impurities and host material.  $\text{CaCl}_2$  and  $\text{MgSO}_4$  will be used as model Mars solutes produced by leaching and weathering. Concentrations will be varied from  $< 1$  mM to 1 M. Chlorine is the most abundant ion that substitutes for oxygen in water ice and increases conductivity, but it saturates in the solid lattice at 3-10 ppm. Excess solutes will form brine channels of differing strengths. Host materials will be varied from  $< 1$  m<sup>2</sup>/g sands taken to be representative of igneous or sedimentary rocks on Mars to  $> 100$  m<sup>2</sup>/g clays that may represent localized environments favorable to biomass accumulation. NMR procedures will be updated to robustly assess unfrozen-water content below 240 K. This work will lead to a better understanding of the limits to habitability near the surface of Mars.