

MAGNETIC RESONANCE AND DIELECTRIC SPECTROSCOPY INVESTIGATIONS OF LIQUID VEIN NETWORKS WITHIN ICE AND ICE-REGOLITH MIXTURES. D. E. Stillman¹, K. P. Primm¹, S. L. Codd², J. D. Seymour², P. Lei², H. G. Sizemore³, R. E. Grimm¹, and A. W. Rempel⁴, ¹Dept. of Space Studies, Southwest Research Institute, Boulder, CO (dstillman@boulder.swri.edu), ²Magnetic Reson. Lab, Montana State University, Bozeman, MT, ³Planetary Science Institute, Tucson, AZ, ⁴Dept. of Earth Sci., University of Oregon, Eugene, OR.

Overview: Unfrozen brines form liquid vein networks (LVNs) when the temperature of a salty solution is below its melting temperature. Furthermore, additional unfrozen liquid water can exist due to interfacial premelting against mineral surfaces when these solutions are frozen in regolith [1-3]. The purpose of our experimental plan is to better characterize: (1) the amount of unfrozen brine, (2) the microscopic location of the brine, and (3) how the tortuosity of the brine changes with temperature, grain size, and salt type and content. These three properties also control the DC conductivity of ice and ice-regolith mixtures. Thus, a major goal of our work is to determine how DC conductivity relates to the three properties of unfrozen brines. Geophysical methods allow low-frequency conductivity of the subsurface to be measured remotely, therefore such measurements on Mars or Europa could be used to determine the amount of brine, its tortuosity, and evaluate habitability of such an environment. Additionally, determining the properties of unfrozen brines will help improve the accuracy of cryosuction modeling on Mars [4].

Background: The amount of unfrozen water ϕ (as porosity) in ice or ice-regolith mixture is a function of temperature, salt type, initial salt concentration, and regolith grain-size distribution. Unfrozen water occurs at a microscopic scale anytime water is frozen within a pore space. As the water freezes into ice, it excludes the majority of the dissolved salts, thus concentrating the unfrozen water into brine. The brine can be found in LVNs at the boundary between two and three ice grains and between ice and the regolith. Colligative effects alone can keep brine from freezing until it is cooled to the eutectic temperature. At the ice-regolith boundary and at grain contacts in LVNs, small volumes of unfrozen water can remain below the eutectic temperature due to interfacial premelting and the Gibbs-Thompson effect.

Magnetic Resonance (MR): MR was used to study ice and ice-regolith samples. Samples were constructed by densely packing monodispersed PMMA (polymethyl methacrylate) particles ($d = 0.4, 10, \text{ or } 102 \mu\text{m}$) in varying solutions of MgCl_2 (30, 60, 120 mM). These samples were measured with two MR techniques known as Carr-Purcell-Meiboom-Gill (CPMG), providing rotational water mobility and Pulse Gradient Spin Echo (PGSE), measuring translational mobility as a function of temperature. The former method allows for quicker measurements on a scale of

minutes and quantitatively measure the unfrozen water porosity ϕ , and qualitatively measures surface-area-to-volume ratio, S/V , of the brine. The latter quantitatively measures ϕ , S/V , and tortuosity α [5], but requires experimental times of hours.

MR measurements are sensitive to S/V of the unfrozen brine and can be used to determine where brine is located. The T_2 (spin-spin relaxation time of a water molecule) distributions are shown for samples with 60 and 120 mM salt concentrations with or without particles after 1 and 3 days of freezing (**Fig. 1**). The data show a population of liquid water at longer T_2 times ($\sim 0.1 \text{ s}$), which indicates this portion of unfrozen water resides in a larger spatial domain (small S/V). Therefore, we assume this population consists of unfrozen water liquid veins between ice grains, possibly at the triple junction (between three ice-grains). An increase in salt concentration leads to more unfrozen water in larger LVN's, thus 120 mM ice has the largest amount of brine in triple junctions, followed by the 60 mM ice sample. With large PMMA beads ($102 \mu\text{m}$), we find that triple junctions still occur as these beads still have large pore sizes. At a moderate PMMA bead size of $10 \mu\text{m}$, we see that only the 120 mM sample is able to possess triple junctions. Furthermore, the 120 mM sample must be aged ~ 3 days to allow recrystallization to create bigger triple junctions. This behavior is consistent with a redistribution of liquid water from particulate surfaces to LVN's, associated with evolution of ice crystals. Conversely, 60 mM at $10 \mu\text{m}$ cannot create triple junctions but must still have considerable unfrozen water because the LVNs must be much thinner than at 120 mM. At a very small PMMA bead size of $0.4 \mu\text{m}$, we detect n

Aging 3 days generates an increase in the T_2 value of the LVN water population in the brine samples consistent with grain growth coarsening partitioning the thermal equilibrium distribution of liquid water in larger veins.

Dielectric Spectroscopy (DS): The complex dielectric permittivity and DC (direct current) conductivity σ of similar ice and ice-regolith mixtures were also investigated. These samples consisted of $d=10 \mu\text{m}$ PMMA particles and quartz (SiO_2) sands of different grain sizes mixed with varying salt types and concentrations measured as a function of temperature. For this research, we focus on how σ is related to tortuosity α via Archie's law [6]: $\alpha = a\phi\sigma_{DC}^{LVN}/\sigma_{DC}^{mix}$, where σ_{DC}^{LVN} and σ_{DC}^{mix} are the conductivity of the LVNs and mixture

and a is a correction coefficient. Note, σ_{DC}^{LVN} is measured, while ϕ and σ_{DC}^{mix} can be modeled. Archie's law can be written differently to also help determine other properties of the sample: $\alpha = a\phi^{1-m}$ where m is the Archie's law exponent, where $m = 1.3, 1.8$, and 3.7 for an unconsolidated, weakly cemented, and strongly cemented matrix, respectively.

Results: Using MR and DS, tortuosity values were determined and fit using Archie's Law (Fig. 2). The Archie's law exponent for MR measurements appear to be much lower than DS measurements, although the 60 mM $MgCl_2$ mixed with the 10 μm beads may indicate higher values of future samples. DS measurements show that ice-regolith mixtures with larger pores formed from spheres $\geq 10\mu m$ have a similar Archie's law exponent to that of the MR measurements. Furthermore, smaller pores have much larger tortuosity values with similar porosity (unfrozen water content). Lastly, MR and DS measurements slightly disagree for the 60 mM $MgCl_2$ mixed with 10 μm beads as the DS measures tortuosity values ~ 20 –30, while MR measures ≥ 100 . Additionally, DS measurements of 60 mM $MgCl_2$ mixed with 10 μm beads are interpreted to possess LVNs with triple junctions.

Future Plans and Conclusions: Through further measurement and analysis, we seek to develop general relations for tortuosity and porosity as functions of salt type and concentration, grain size, and temperature, and to use these dependent quantities to infer where cryosuction is an efficient water-transport mechanism on Mars.

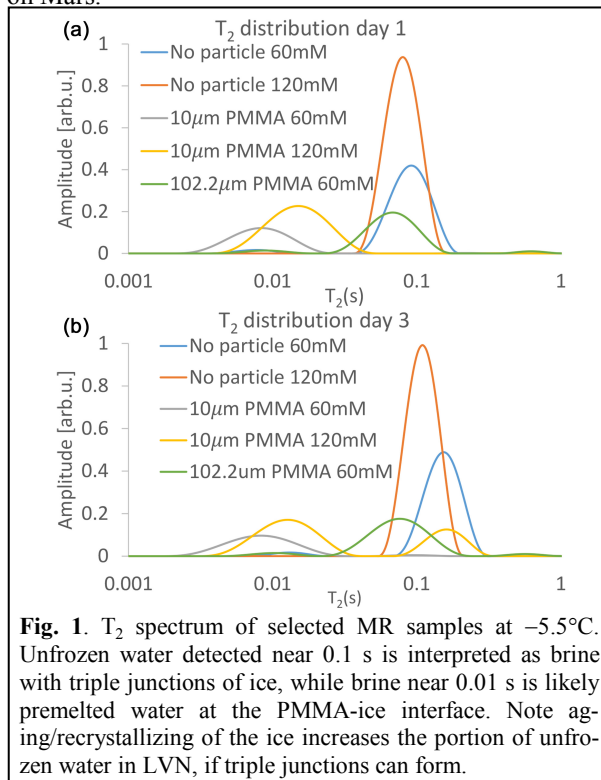


Fig. 1. T_2 spectrum of selected MR samples at $-5.5^\circ C$. Unfrozen water detected near 0.1 s is interpreted as brine with triple junctions of ice, while brine near 0.01 s is likely premelted water at the PMMA-ice interface. Note aging/recrystallizing of the ice increases the portion of unfrozen water in LVN, if triple junctions can form.

References: [1] Rempel (2012) *Vadoze Zone J.*, 11, vzj2012.0045. [2] Rempel et al. (2004) *J. Fluid Mech.* 498, 227–244. [3] Wettlaufer & Worster (2006) *Annu. Rev. Fluid Mech.* 38, 427–452. [4] Sizemore et al. (2015) *Icarus*, 251, 191–210. [5] Sen (2004) *Concepts in Magn. Res.*, 23A, 1–21. [6] Stillman et al. (2010) *J. Phys. Chem. B*, 114, 6065–6073.

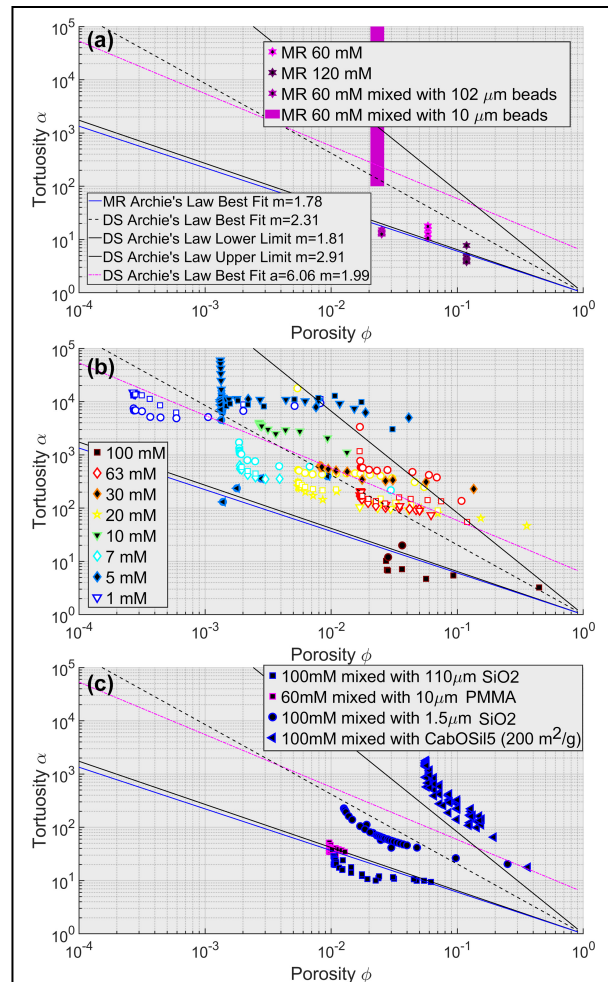


Fig. 2. Tortuosity as a function of porosity as measured by (a) MR techniques, (b) DS techniques of ice samples, and (c) DS techniques of ice-regolith samples. Note the best fit of each plot is shown on all the plots to compare between the different techniques and samples and all concentrations are mM of $MgCl_2$. (a) MR measurements show the tortuosity of samples at $-5.5^\circ C$. The first three samples fit Archie's law with an $m=1.78$ (blue fit), which would signify a weakly cemented matrix. The other sample (60 mM $MgCl_2$ with 10 μm PMMA beads) registered a tortuosity that was greater than 100. (b) DS measurements of the tortuosity of LVNs in ice show significant scatter. Assuming $a=1$, we find the range of Archie's law exponent to be $m=1.81$ – 2.91 (black dashed fit). The lower value of this range best corresponds to the MR range. Fitting an Archie Law where a is allowed to vary, produces the magenta line. (c) DS measurements of the tortuosity of LVNs in ice-regolith mixtures span a similar range of the ice measurements, but vary in a logical way. As large pore sizes allow for smaller tortuosity values with decreasing porosity, smaller pores create larger tortuosity values.