**CRYOGEOCHEMISTRY: LIQUID WATER IN UNEXPECTED PLACES.** L. M. Anovitz[1], A. H. Treiman[2], E. Mamontov[3], A. I Kolesnikov[3], A.G. Stack[1], D. R. Cole[4] and D. J. Wesolowski[1], [1]Chemical Sciences Division, MS 6110, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6110, United States, anovitzlm@ornl.gov, [2]Lunar and Planetary Institute 3600 Bay Area Boulevard, Houston, TX 77058 treiman@lpi.usra.edu, [3]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6473, United States mamontove@ornl.gov kolesnikovai@ornl.gov. [4]School of Earth Sciences, The Ohio State University, Columbus, OH, USA

**Introduction:** To a reasonable approximation, reactions in aqueous systems stop at temperatures where water is frozen. The slow diffusion or other transport rates possible in the solid state dramatically retard ionic or mineral/fluid reactions. While it is well known that saline brines freeze at temperatures well below those of liquid water (e.g. -21.1°C for 23.3 wt % NaCl in $H_2O$). The magnitude of such freezing point depression depends on the nature and concentration of the salts involved.

However, it has also been shown by several authors[1-8] that the freezing point of a confined liquid is also a function of the size and composition of the pore within which it is located. In part this is due to the Gibbs-Thompson effect, and will be true for any small droplet, but it is also a function of the confinement of the fluid within the pore which alters the physical-chemical nature of the fluid compared to the bulk solution (e.g., the electrical double layer, density, phase behavior).

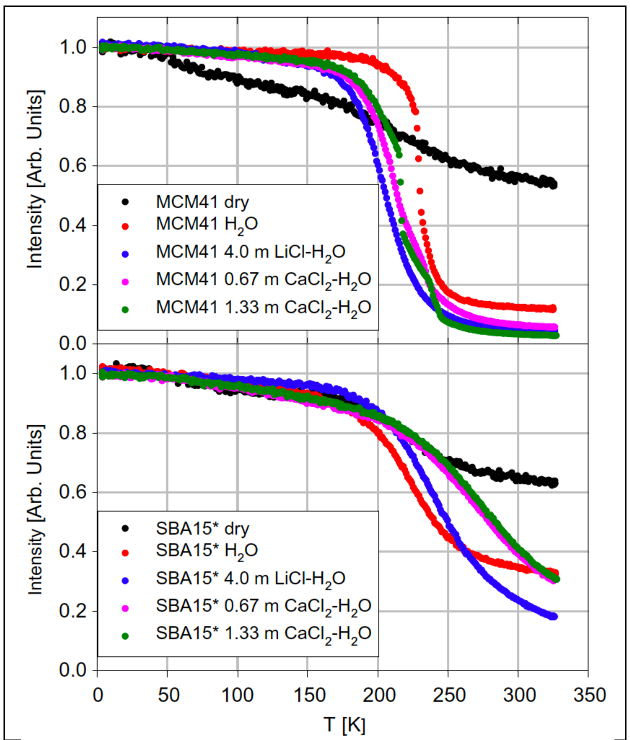


Figure 1: The results of the neutron elastic scattering intensity scans summed for 0.62 Å_1 < Q < 1.68 Å_1 for water and solutions confined in MCM41 and SBA15*. The spectra have been normalized to the intensities measured at 5 K. [2]

This property of nanoconfined fluids has significant implications for aqueous chemistry in extraterrestrial bodies. As the freezing point of an aqueous fluid can be depressed significantly in small pores, <u>liquid</u> water or brines can, therefore, exist in rocks in such bodies under conditions where bulk water would freeze. Thus, aqueous chemical reactions can also proceed, however

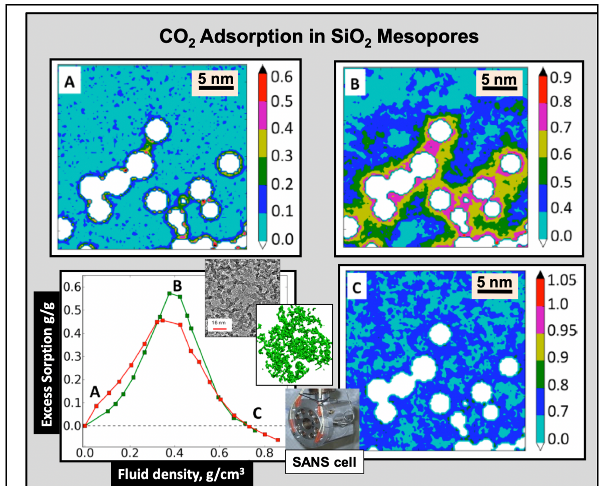


**Figure 2:** 2D density profiles (g/cm³) of $CO_2$ confined in a silica aerogel matrix (average pore size ~14 nm) corresponding to different stages of pore filling at 35 °C calculated from Grand Canonical Lattice Gas simulations. The white areas represent thin strands of the silica matrix. The letters indicate corresponding states in the 2D profiles and in a plot of excess sorption as a function of bulk $CO_2$ density (bottom left) obtained from experiment (red) and modeling (green) for $CO_2$ in silica aerogel with a density of 0.1g/cm³. Excess adsorption is the difference between the amount of fluid in the system and the amount that would be present at the same T and P in the absence of adsorption. Inserts include a TEM image of the silica (scale bar = 16 nm), a mathematical rendering of this material (green) generated from diffusion-limited cluster-cluster aggregation based on TEM images, and the high P-T experimental SANS cell used. The results demonstrate that density changes in concert with pore size and pore throats are critical in driving pore fluid condensation. [9,10]

slowly. Furthermore, as the density of fluids under confinement can also be significantly higher than under the same pressure and temperature conditions for bulk water, [9,11] and as solubility is usually a positive function of fluid density [12] these changes may enhance reactivity and transport (Figure 2). Conversely, some studies also show that the density of confined water may be less than that of the bulk (Figure 3).[13] While the pore scales involved are generally too small for earth-like organisms, the potential effects of this chemical environment on extraterrestrial life are unknown.

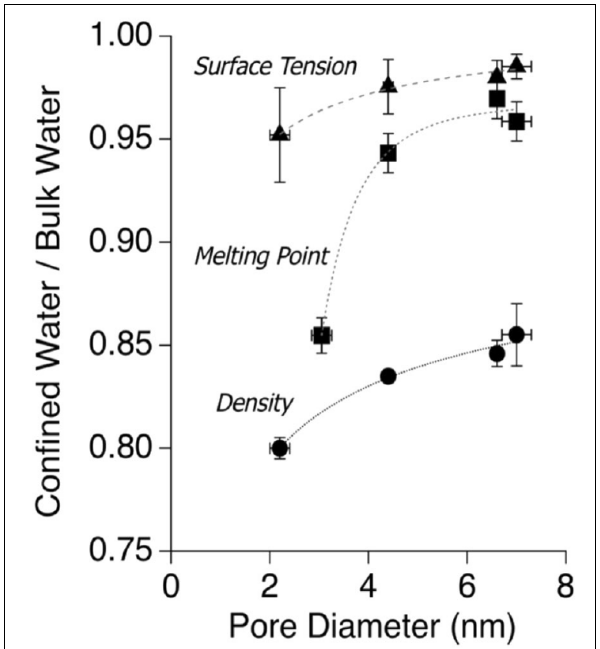


Figure 3: The calculated relative surface tension and density, determined by BET $N_2$ and water adsorption studies, along with the relative melting point, determined by differential scanning calorimetry, versus silica pore radius (Knight et al., 2019).

**Discussion**: An example of the effects of confinement of freezing is shown in Figure 1, which displays the results of elastic scans for a series of brines and pure water confined in two synthetic zeolites (MCM-41 and SBA-15) performed on the HFBS Quasi-elastic neutron spectrometer (QENS) at the NIST Center for Neutron Research (NCNR, Mamontov et al., 2008). The synthetic zeolites were used because of their well-defined pore sizes (2.7 nm in MCM-4, and 1.4 nm in SBA-15). In QENS measurements all the intensity is expected to occur in the elastic part of the spectrum below freezing. The onset of diffusion dynamics, that is, of melting, transfers intensity away from the elastic line. As neutrons are both very penetrating through most solids, and very sensitive to motions of hydrogen, and thus water, the elastic intensity can be used to determine the onset of melting in nanopores.

As can be seen in Figure 1, the nature of confinement-induced freezing point depression is a function of the size and composition of the pore. Anovitz et al. [14] showed, for instance, that when the pores are very small, such as the ~0.5 nm diameter channels in beryl, freezing does not occur at all. The scale at which confinement affect becomes significant may also depend on the size of the confined molecule, being greater for large organic complexes.

To date, the implications of fluid confinement of the chemistry of extraterrestrial systems remain unexplored. However, it seems likely that they imply the potential presence of liquids under conditions that would otherwise not have been considered possible. By extension, water and brine present in nanopores may suggest an alternative strategy of where to search for water on Mars.

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