THE EXPERIMENTAL FORMATION OF LONG-LIVED SUPERCOOLED BRINES DOWN TO –120°C ON MARS. J. D. Toner[1] and D. C. Catling[1], [1]University of Washington, Dept. of Earth and Space Sciences/ cross-campus Astrobiology Program, 4000 15th Avenue NE, Seattle, WA, 98195 (toner2@uw.edu).

Introduction: Liquid water is possible on the cold and dry surface of Mars where concentrated salt solutions lower the freezing point of water. The maximum equilibrium freezing-point depression possible is known as the eutectic temperature (T_e): –34°C, –57°C, and –75°C for $NaClO_4$, $Mg(ClO_4)_2$, and $Ca(ClO_4)_2$ respectively. However, Toner et al. [1] found that salt solutions will typically supercool by about 15°C before crystallizing, and that $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ supercool down to –120°C, forming an aqueous glass. Low-temperature glasses are significant because the cryopreservation of microbes in glasses allows frozen microbes to remain viable after rewarming, which may enable extremophile forms of life to persist at extremely low temperatures.

Toner et al. [1] studied supercooling in pure solutions and in soil-solution mixtures using binary salt solutions (a single salt added to water). In this study, we extend the study of Toner et al. [1] by measuring supercooling in binary and ternary mixtures in the Na-Mg-Cl-ClO_3-ClO_4-NO_3-SO_4-H_2O system in the presence of ice. We report a new discovery that mixtures of chlorate (ClO_3), perchlorate (ClO_4), and nitrate (NO_3) salts, as well as Mg-SO_4-(ClO_3,ClO_4) mixtures, do not crystallize completely, even during slow cooling/warming rates (1°C min^{-1}) and repeated temperature cycling. Instead, these mixtures form low-temperature aqueous glasses at temperatures ranging between –90°C to –115°C.

Methods: We use Differential Scanning Calorimetry (DSC) to measure supercooling and phase transitions in low-temperature aqueous solutions. A DSC identifies phase transitions by measuring the heat flux in a sample relative to an inert reference material as the sample is warmed or cooled at a constant rate. To analyze a sample, we pipet ~50 μL of solution into a sample pan, cool the sample down to –140°C, and then warm the sample at a constant rate to 0°C. T_e of a sample is identified by a large endothermic spike in the heat-flux trace, and the glass transition (T_g) is indicated by a characteristic increase in the sample heat capacity as the sample transitions from a glass to a liquid.

The initial concentration of our solutions is about 0.1 molal. Upon cooling, solutions crystallize ice at about –20°C, which concentrates the remaining solution into a brine. A eutectic mixture results when salts also precipitate and the entire sample has crystallized. These experiments on icy solutions are relevant to freezing processes in ice-rich soils found near the polar regions of Mars.

Results:

Binary salt solutions. All of the binary salt solutions we investigated in the Na-Mg-Cl-ClO_3-ClO_4-NO_3-SO_4-H_2O system crystallize to form a eutectic mixture of salt and ice. We find that the eutectic of $Mg(ClO_4)_2$ is –57°C, in agreement with recent studies [1,2]. All other binary salt solutions have eutectics consistent with previous studies [3].

Ternary salt solutions. Ternary salt mixtures commonly have a eutectic slightly lower than the salt component having the lowest eutectic. For example, we find that eutectic of a Mg-Cl-ClO_4 mixture is –60.9°C vs. –57°C for $Mg(ClO_4)_2$. However, a number of solutions never crystallize salt, but instead form a mixture of ice and glass. Solutions that do not crystallize salt include (Mg,Na)-(ClO_3,ClO_4,NO_3) and Mg-SO_4-(ClO_3,ClO_4) mixtures. Remarkably, even mixtures of relatively high eutectic salts, such as Na-ClO_3-NO_3 (T_e $NaClO_3$ = –24.9°C and T_e $NaNO_3$ = –17.5°C) do not crystallize salt. These results suggest that long-lived low-temperature liquid water should form on Mars in ice-rich supercooled brine mixtures.

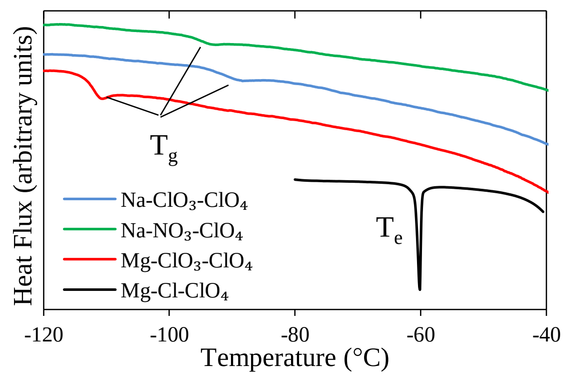

Fig. 1. Heat flux traces for selected ternary salt mixtures, indicating features due to melting at the eutectic temperature (T_e) and the glass transition temperature (T_g). The slow increase in the heat flux with temperature is due to ice melting.

Acknowledgements: Funding from NASA Mars Data Analysis grant #NNX10AN66G to D. Catling, a NASA Astrobiology Institute Postdoc awarded to J. Toner, and a Univ. of Washington Royalty Research Fund Award to purchase the DSC.

References: [1] Toner, D. D. et al. (2014) *Icarus, 233*, 36–47. [2] Stillman and Grimm (2011) *JGR, 116*. [3] Marion et al. (2010) *Icarus, 207*, 675–685.