**WHAT SALTS ACTUALLY FORM IN MARTIAN SOILS?: EXPERIMENTAL RESULTS USING DIFFERENTIAL SCANNING CALORIMETRY.** J. D. Toner[1] and D. C. Catling[1]
[1]University of Washington, Dept. Earth & Space Sciences and Astrobiology Program, Seattle, WA 98195, USA. (e-mail: toner2@uw.edu)

**Introduction:** Perchlorate ($ClO_4^-$) has been detected in several locations on Mars in relatively high concentrations (compared to Earth deserts [1,2]) and is thought to be globally distributed in soils [3,4]. The presence of perchlorate on Mars has attracted considerable interest because (1) aqueous perchlorate solutions can remain liquid down to –75°C and will spontaneously absorb atmospheric water to form brines, which may support extremophile forms of life [5,6], (2) perchlorate brines can supercool relatively easily and form aqueous glasses near –120°C [7], (3) hydrated crystalline perchlorate salts can sequester significant amounts of water in their crystal structure, and (4) perchlorates are toxic to humans, which may complicate future human exploration of Mars.

Prior to their initial detection by the Mars *Phoenix Lander* [8], perchlorates had not been extensively studied owing to their rarity on Earth [1,2]. After the detection of perchlorate on Mars, a number of studies have addressed this knowledge gap using both experimental [e.g. 6] and equilibrium modeling approaches [e.g. 7, 9]. However, perchlorates remain poorly characterized at low temperatures. For example, critical equilibrium properties, such as the eutectic temperature and hydration state of $Mg(ClO_4)_2$ salts remain uncertain. Attempts to understand perchlorates are complicated by the slow kinetics of crystallization at low temperatures, which results in the formation of metastable solutions [6,7]. We also note that very few studies have investigated mixtures of perchlorates with other salts [9,10].

Our goal in this study is to better understand what salts precipitate from perchlorate-rich solutions on Mars by analyzing phase transitions in simulated Mars soil-solutions using a Differential Scanning Calorimeter (DSC). Such measurements can be used to 'ground-truth' equilibrium model predictions, identify new or metastable salt phases, and predict what salt phases are present in Mars' soils.

**Methods:**

*Differential Scanning Calorimeter (DSC)*. 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. The onset temperature of a phase transition is indicated by a heat flux peak in a DSC analysis, and transition enthalpies can be calculated from the area under the peak. Our DSC is cooled by liquid nitrogen and is capable of continuous heat flux measurements from –170°C to >25°C. Furthermore, our DSC can cool or warm samples at rates ranging from less than 0.1 K $min^{-1}$ to >50 K $min^{-1}$. The slow rates of temperature change are relevant to diurnal temperature changes on the surface of Mars, which has a maximum rate of surface temperature change ~0.2 K $min^{-1}$.

To analyze a sample, we weigh ~10 mg of soil simulant into an aluminum DSC sample pan, and then pipet in ~10 μL of salt solution. The sample pan is then hermetically sealed, which prevents the solution from evaporating over the course of the DSC analysis. We are currently using fine-grained silica sand as our soil, but will also use a Mars soil simulant in the future. Our salt solutions range from saturated solutions at 25°C to dilute solutions.

Our analysis of perchlorate solutions is focusing first on pure solutions of $NaClO_4$, $Ca(ClO_4)_2$, and $Mg(ClO_4)_2$. Following this, we then plan to investigate more complex ($SO_4$, Cl, $ClO_3$, $NO_3$)-$ClO_4$ mixtures. Ultimately we will measure phase transitions in a nominal Wet Chemistry Laboratory (WCL) solution as measured by the *Phoenix Lander*.

**DSC Analysis Results:** Our DSC results indicate that there are a number of previously uncharacterized phase transitions in $NaClO_4$, $Ca(ClO_4)_2$, and $Mg(ClO_4)_2$ solutions (Fig. 1). All solutions show a large endothermic heat-flux peak at previously determined eutectic temperatures: $NaClO_4$ (–34°C), $Ca(ClO_4)_2$ (–76°C), and $Mg(ClO_4)_2$ (–57°C). However, at higher temperatures, our DSC results show several unexpected phase changes. Saturated $NaClO_4$ solutions show two phase transitions at –19 and –3°C, which are not associated with any known transitions in the $NaClO_4$ system. Furthermore, we find that phases in the $NaClO_4$ system are highly dependent on previous temperature programs; different heat flux peak occur in saturated $NaClO_4$ solutions when the temperature is repeatedly cooled and warmed. Saturated $Ca(ClO_4)_2$ shows two endothermic phase transitions at –17.8 and –2.2°C, followed by an exothermic peak near 3°C. Again, the cause of these phase changes is presently unknown. In saturated $Mg(ClO_4)_2$ solutions, a large endothermic peak at –47°C indicates another previously unknown transition. Phase transitions in lower concentration solutions are generally consistent with known transitions (Fig. 2). The melting point of ice is indicated by a sharp endothermic peak, which is well correlated with known freezing-point depressions (FPDs). This suggests that DSCs can be used to rapidly measure FPDs.

**Conclusions:** We have measured phase changes in perchlorate solutions and found a number of previously unknown transitions. Although the hydration states and structure of the phases responsible for many of our measured transitions are presently unknown, there are ways to determine these, and our study provides a roadmap for future investigation on perchlorate salt systems. Our future work will focus on measuring perchlorate mixtures by DSC, and analyzing the heat flux traces we have measured so far to determine enthalpies associated with our phase transitions.

**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] Catling D. C. et al. (2010) JGR, 115, E00E11. [2] Kounaves S. P. et al. (2010) *JGR*, 115, E00E10. [3] Navarro-González, R., E. et al. (2010), *JGR*, 115, E12010. [4] Leshin, L. A., et al. (2013), *Science*, 341, 6153. [5] Marion G. M. et al. (2010) *Icarus*, 207, 675-686. [6] Gough, R. V. et al. (2011), *EPSL*, 312(3-4), 371–377. [7] Toner, J. T. et al. (2013), *Icarus*, 233, 36–47. [8] Hecht M. H. et al. (2009) *Science*, 325, 5936. [9] Toner, J. T. et al. (2015), *Icarus*, in press. [10] Gough et al. (2014), *EPSL*, 393, 73–82.

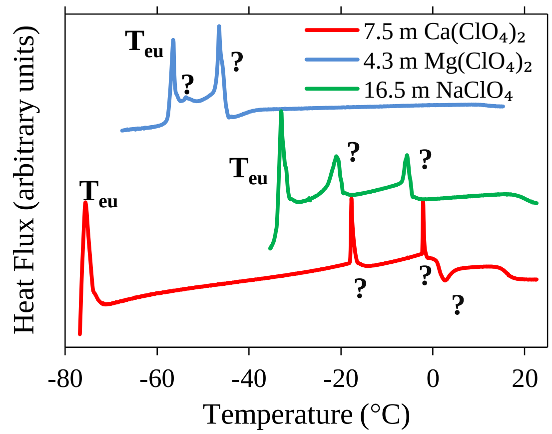


Fig. 1. Heat flux traces for saturated $NaClO_4$, $Mg(ClO_4)_2$, and $Ca(ClO_4)_2$ soil-solutions measured with our DSC during a 5 K min$^{-1}$ warming ramp after cooling to –80°C. Note: a positive heat flux indicates an endothermic event, and a negative heat flux indicates an exothermic event. Peaks due to eutectic melting of an ice/salt mixture are indicated ($T_{eu}$). Peaks due to previously uncharacterized phase transitions are indicated by question marks (?).

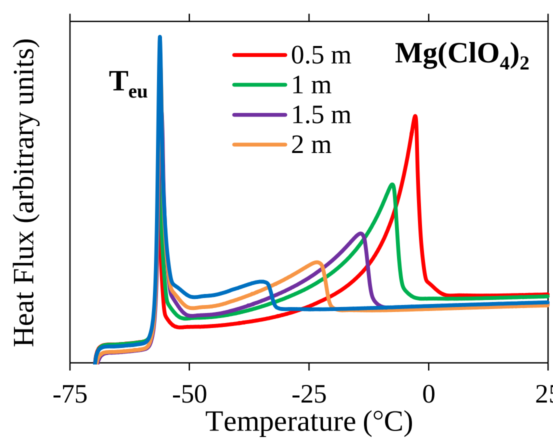


Fig. 2. Heat flux traces for different concentration $Mg(ClO_4)_2$ solutions. Note: a positive heat flux indicates an endothermic event, and a negative heat flux indicates an exothermic event. Peaks due to the eutectic are indicated by $T_{eu}$, which occurs at –57°C. All other peaks are due to the melting point of ice.