

**CREEP OF WATER ICE PLUS MAGNESIUM PERCHLORATE HYDRATE.** H. J. Lenferink<sup>1</sup>, W. B. Durham<sup>1</sup>, A. V. Pathare<sup>2</sup>, L. A. Stern<sup>3</sup>, D. E. Stillman<sup>4</sup>, <sup>1</sup>Massachusetts Institute of Technology ([hendrik@mit.edu](mailto:hendrik@mit.edu)), ([wbdurham@mit.edu](mailto:wbdurham@mit.edu)), <sup>2</sup>Planetary Science Institute ([pathare@psi.edu](mailto:pathare@psi.edu)), <sup>3</sup>U. S. Geological Survey, Menlo Park ([lstern@usgs.gov](mailto:lstern@usgs.gov)), <sup>4</sup>Southwest Research Institute ([dstillman@boulder.swri.edu](mailto:dstillman@boulder.swri.edu))

**Introduction:** Motivated by the discovery of perchlorate ( $\text{ClO}_4$ ) in the Mars northern polar layered deposits by the Phoenix lander [1], and an ice cap morphology that suggests a material of weaker rheology than ice (e.g., *Fisher et al.* [2]; *Koutnik et al.* [3]), we initiated a laboratory investigation of the rheological behavior of icy mixtures containing perchlorate. Reported here are the results of an exploratory experiment in which we deformed a polycrystalline sample of solid ice +  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  of eutectic composition (mass fraction  $\text{H}_2\text{O} = 0.44$ ; melting  $T = 206 \text{ K}$  [4, 5], more recently measured as  $216 \text{ K}$  [16]). We found the material to be profoundly weaker than pure water ice at Mars polar cap temperatures.

The Wet Chemistry Laboratory (WCL) aboard Phoenix mixed three Martian soil samples with water, yielding aqueous solutions containing approximately 0.01 moles of dissolved salts with an average of 0.5% perchlorate by mass leached from each sample [1, 6]. Additional evidence for perchlorate is provided by Phoenix's Thermal and Evolved Gas Analyzer (TEGA), which measured the production of Mass 32 over a temperature range consistent with molecular oxygen ( $\text{O}_2$ ) production due to perchlorate salt decomposition [1, 7]. Since the eutectic temperature for 44.0 wt% magnesium perchlorate is 206-216 K [4], the presence of perchlorate hydrates may lead to liquid brine formation under present-day Martian conditions [1, 5, 8]. Furthermore, *Colling et al.* [9] show via photochemical modeling of the Mars analog Atacama desert that the origin of Martian perchlorate may be atmospheric oxidation, which suggests that perchlorate may be a component of not just soil but also ice on Mars (e.g., *Fisher et al.* [2]).



Figure 1. Indium-jacketed polycrystalline ice+perchlorate sample (a) after hydrostatic compaction and (b) after deformation. Right-cylindrical shape indicates a well-behaved experiment. For scale, diameter of column is 25 mm.

**Experiments:** The material tested was solid ice +  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  of eutectic composition (mass fraction  $\text{H}_2\text{O} = 0.44$ ; melting  $T = 206 \text{ K}$  [4, 5], which we synthesized by freezing from the liquid, then annealing at slightly subsolidus temperatures ( $212 \text{ K}$ ). We pulverized cold material and packed it into a cylindrical indium jacket, then hydrostatically pressurized the material at  $100 \text{ MPa}$  to remove all porosity (Fig. 1) and to promote crystallinity. Preliminary x-ray diffraction indicates that the starting material was indeed crystalline. We then deformed the sample in 3 steps, at  $180 \text{ K}$ ,  $190 \text{ K}$ , and  $195 \text{ K}$ , to a total strain of 0.13, with results shown in Fig. 2. Stress vs. strain rate did not appear to evolve with strain following a brief (1 – 2% strain) transient period after condition stepping, but proof of steady state requires further experimentation.

**Results:** The eutectic mixture is far weaker than pure water ice at these temperatures, and its strength has a temperature sensitivity that is much more pronounced than that of ice. At  $195 \text{ K}$ , viscosity is a factor of  $>10^3$  lower than that of pure ice at the same temperature under the same stress. Presumably the viscosity contrast will continue to widen as temperature approaches the eutectic. Cryogenic scanning electron microscope (CSEM) imaging reveals an intermeshed fine structure of ice and perchlorate hydrate (Fig. 3) similar to what we have seen in eutectic mixtures of hydrated sulfate salts and ice [10]. The flow behavior here is very similar to that in the system  $\text{H}_2\text{O}-\text{NH}_3$ , which has an even deeper eutectic melting near  $176 \text{ K}$ .

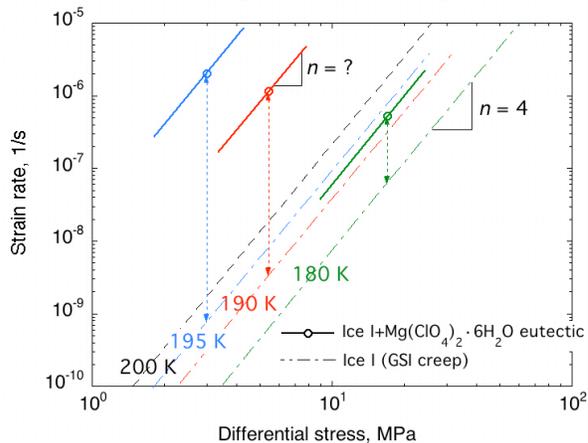


Figure 2. Creep of Mg perchlorate eutectic, based on a 3-step deformation experiment (circles), compared with the flow law for pure ice in GSI creep (dash-dot lines). The perchlorate is far weaker than ice, and the difference increases with increasing  $T$ . At  $195\text{-K}$ , the viscosity contrast at  $3 \text{ MPa}$  stress is over 3 orders of magnitude (dashed arrows).

[11]. The viscosity of eutectic composition material in that system, near that of pure  $\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , is so temperature sensitive that it passes from essentially zero at 176 K to being isoviscous with ice at 143 K.

**Ongoing work.** Having established that the presence of perchlorate has the potential to significantly weaken an ice formation, we aim to provide quantita-

tive definition of that weakening. Deformation experiments on eutectic composition material will allow us to quantify activation energy and stress sensitivity and to establish that the measured behavior does indeed apply to steady state flow. We will explore as close as possible to the eutectic melting temperature.

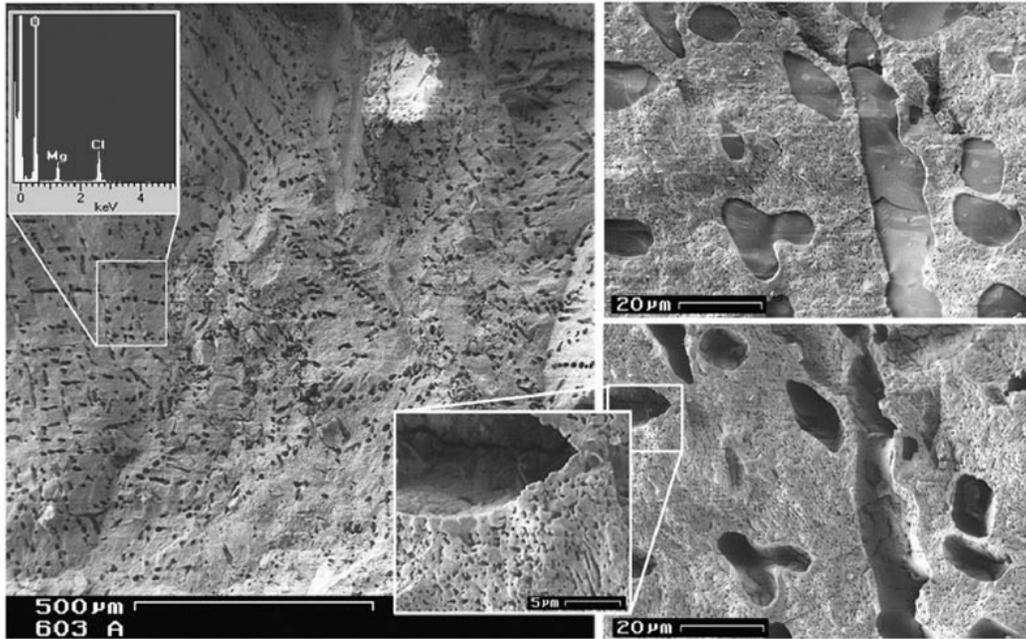


Figure 3. Ice + Mg perchlorate hydrate eutectic texture after deformation. Low-magnification CSEM image at left shows Mg perchlorate after the ice has sublimated. Here, ice originally occupied all the open channels and holes seen along the surface, distributed in a loosely uniform manner and with channels often spaced  $\sim 50$  microns apart. Energy-dispersive x-ray scans of the remaining solid phase confirms oxygen, magnesium, and chlorine as the only measurable elements in the spectra (box at top left.) SEM images at right show a section of sample after minor sublimation (top) and full sublimation (bottom) of the ice. Many of the ice pods are in fact isolated rather than interconnected below the surface. Images were taken at  $T < 85\text{K}$  and vacuum below  $10^{-5}$  mbar.

Future experiments will also explore the rheological behavior of two related compositions. Given the low expected bulk concentration of perchlorate in the NPLD [9], we will investigate possible doping effects on flow of ice of millimolar concentrations of the same perchlorate, in the event that there has been no significant geological concentration of perchlorate. We also plan to look for rheological effects upon water ice of hydrogen peroxide, which numerous workers have suggested may be widespread on Mars (e.g., *Encrenaz et al.* [12]; *Hurowitz et al.* [13]; *Zahnle et al.* [14]). In summary, our goal is help evaluate the likelihood of (a) glacial sliding due to softening at the base of the NPLD as envisioned by *Fisher et al.* [2], and (b) enhancement throughout the NPLD resulting from impurities (such as perchlorate and hydrogen peroxide) that *Koutnik et al.* [3] suggest may be required to explain the morphometric evidence for glaciation in Gemina Lingula [15].

**References:** [1] M. H. Hecht et al. (2009) *Science*, 325, 64. [2] D. A. Fisher et al. (2010) *J. Geophys. Res.-Planets*, 115. [3] M. R. Koutnik et al. (2010) paper presented at the 41st Lunar and Planetary Science Conference, Abstract #2272. [4] V. F. Chevrier et al. (2009) *Geophys. Res. Lett.*, 36. [5] G. M. Marion et al. (2010) *Icarus*, 207, 675. [6] S. P. Kounaves et al. (2010) *J. Geophys. Res.-Planets*, 115. [7] W. V. Boynton et al. (2009) *Science*, 325, 61. [8] M. P. Zorzano et al. (2009) *Geophys. Res. Lett.*, 36. [9] D. C. Catling et al. (2010) *J. Geophys. Res.-Planets*, 115. [10] C. McCarthy et al. (2007) *American Mineralogist*, 92, 1550. [11] W. B. Durham et al. (1993) *J. Geophys. Res.*, 98, 17667. [12] T. Encrenaz et al. (2004) *Icarus*, 170, 424. [13] J. A. Hurowitz et al. (2007) *Earth Planet. Sci. Lett.*, 255, 41. [14] K. Zahnle et al. (2008) *J. Geophys. Res.-Planets*, 113. [15] D. P. Winebrenner et al. (2008) *Icarus*, 195, 90. [16] D. E. Stillman and R. E. Grimm, this meeting.