A TEMPERATURE-CONTROLLED SAMPLE STAGE FOR MICRO-X-RAY DIFFRACTION OF MIRABILITE-CONTAINING SAMPLES FROM WOLF SPRING, AXEL HEIBERG ISLAND, NUNAVUT, CANADA. M. S. Bramble[1], R. L. Flemming[2], J. L. Hutter[1], [1]Dept. of Physics and Astronomy, and the [2]Dept. of Earth Sciences, University of Western Ontario, London, ON, Canada, N6A 5B7 (mbramble@uwo.ca).

Introduction: Mineral precipitates brought back from a perennial saline cold spring at Wolf Spring, Axel Heiberg Island, Nunavut, underwent visible changes in their mechanical properties upon equilibrating with ambient laboratory conditions [1]. The returned samples, collected from areas around the vent of Wolf Spring, were identified by powder X-ray diffraction (pXRD) at ambient laboratory temperature to contain thenardite (Na_2SO_4) as a major phase [1]. Mirabilitie ($Na_2SO_4{\cdot}10H_2O$) was identified as a minor and trace phase, but observations made on-site suspect mirabilite to be a more substantial phase in the year-round, subzero spring than suggested by pXRD [1]. Mirabilite is known to dehydrate to thenardite, thus changing its crystal structure and mechanical properties, in the range of temperatures and humidity experienced during transition from the –25 °C storage to the ambient laboratory environment [2]. In order to perform XRD analysis of the samples in an environment representing *in situ* temperature conditions, a temperature-controlled (TC) sample stage was designed and built for use with a micro-X-ray diffractometer (µXRD). A TC stage would allow the phases present at low temperature to be identified by their crystal structures at any temperature between –25 °C and ambient conditions.

Temperature-Controlled Sample Stage: In this study, a TC sample stage was developed which enables X-ray diffraction of minerals within a range of temperatures from ~ –45 to 85 °C, and having a range of mineral grain sizes and textures.

In situ µXRD has been shown to be an effective method for identifying mineral phases and textures present in geological and planetary samples [3]. For hydrated minerals, µXRD is particularly advantageous because mechanically destructive sample preparation is not required prior to analysis. Powdering mirabilite has been observed to induce dehydration even under constant temperature and humidity. Adding a TC stage to the µXRD extends the capabilities of this instrument to analyse a wide variety of materials at non-ambient temperatures.

The TC stage (Fig. 1) featured a single stage thermoelectric (TE) module (Marlow Industries DT12-8-01) with cooling face dimensions of 40 x 40 mm and a maximum ΔT of 66 °C while operating at a temperature of 27 °C. This Peltier-effect module was connected to a temperature controller (Tellurex TTC-12-24A) with a power supply module (Tellurex PS-12-12) that provided 12 V DC at 12 A output allowing for the full range of operation of the 7.4 A module.

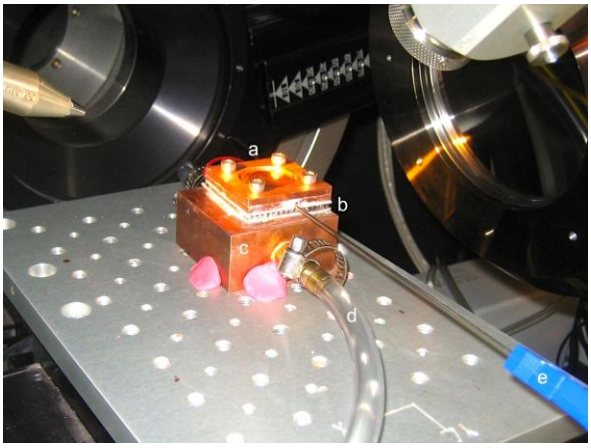

Figure 1: The TC stage mounted on the XYZ stage of the µXRD. The a) sample holder, b) TE module, c) heat sink, d) water hosing, and e) thermocouple are visible in this image.

The sample holder consisted of two parts: a 40 x 40 x 3 mm block of copper which contacted the TE module, and a copper plate containing a 1 mm depression 25 mm in diameter to contain the sample. This copper block had a hole bored to the centre to accommodate a temperature sensor and four threaded holes to allow the sample holder to be fastened to the bottom block, ensuring a good thermal contact. As with the TE / copper block contact, a layer of thermal paste separated the bottom block from the sample holder.

A quick-disconnect thermocouple (Omega Engineering, Inc., TMQSS-062U-6) was inserted into a 1.6 mm hole bored into the sample holder bottom block, to provide temperature information from the sample holder to the temperature controller. This temperature sensor was coated with a layer of thermally conductive paste prior to injection, and the same thermal paste coated each side of the TE module.

The hot side of the TE module was placed in contact, via a layer of thermal paste, with a heat sink consisting of a 51 x 51 x 25 mm copper block. A 12.7 mm hole with threaded-in copper hose couplings on each end passed through the heat sink. Using hose clamps, the system was plumbed into the enclosure using 15 m of tubing connected to an open water source and drainage. This dissipated heat via a flow of water at ~4 litres per minute.

To prevent ice crystals from forming on the sample and sample holder due to condensation, a continuous

flow of nitrogen gas was directed towards the centre of the sample. The gas was piped in directly from a cylinder outside the enclosure and was spread about the sample via a baffle ~10 cm away from the sample.

The University of Western Ontario's Bruker D8 Discover µXRD with a radiation source of CoKα (1.78897 Å) was used for this investigation, operating at 35 kV and 45 mA. Data were collected with a two-dimensional General Area Detector Diffraction System (GADDS), and the TC stage was placed atop a remote-controlled XYZ sample stage.

For data collection, one GADDS frame was collected using omega scan mode, with the parameters $\theta_1 + \theta_2 = 36°$, with $\theta_{1(start)} = 10°$ and $\theta_{2(start)} = 26°$, and scanning through an omega angle of $\omega = 14°$. A 300 µm nominal beam diameter was used, together with XY oscillation of the sample by 2 mm to maximize the number of crysallites in the dataset, somewhat akin to bulk powder XRD of the sample.

Demonstration Experiment: The performance of the stage was demonstrated through the analysis of a synthetic sample of the mirabilite (Sigma-Aldrich 403008-100G) held at –25 °C and then incrementally warmed to ambient laboratory temperatures during the acquisition of *in situ* diffraction data. No phase changes were seen in the mirabilite (XRD spots) during the ~2 hours held at –25 °C (compare Figs. 2a & 2b) despite the µXRD enclosure being at ambient temperature and humidity. However, the amount of secondary thenardite (polycrystalline Debye rings) increased (compare Figs. 2a & 2b). Beginning at 0 °C and continuing until thermal equilibration at ambient laboratory temperatures, mirabilite was observed to undergo a phase transformation to thenardite upon dehydration.

After warming above 0 °C, trace amounts of water entered the sample holder from the melting of condensation ice crystals around the edge of the holder. The presence of water in contact with portions of the sample caused both thenardite and mirabilite to crystallize <5 µm crystals in the sample holder during the warming from 0 to 23 °C (yielding rings, Fig. 2c). At ambient conditions, mirabilite completely dehydrated; only polycrystalline thenardite remained (Fig. 2d).

The presence of the melt water may have altered the phases present between 0 °C and ambient temperatures, suggesting that data collected in this temperature range (~ 0 – 20 °C) should not be given much consideration in relation to phases present in the Wolf Spring samples, as the data may not reflect changes occuring on location. The focus of the cold stage in its current setup should be on bulk identification at sub-zero and ambient temperatures.

In a subsequent experiment, the top of the sample holder was beveled to a small angle (~3°) so that, when warming above 0 °C, the water generated by the melting of condensate ice crystals would be directed away from the sample and towards the edges of the cold stage. This solution did not completely remove the issue with water in the sample holder when warming above 0 °C, likely because the samples contain a thin coating of water ice crystallised from water vapour in the sample tubes and bags during transport and storage.

Ongoing Study and Conclusion: Preliminary data collected from the Wolf Spring samples show mirabilite present in a number of samples at sub-zero temperatures, which dehydrates and is not detected once the sample equilibrates to ambient laboratory conditions. Certain phases—halite, thenardite, and gypsum—are present throughout the data collection at all temperatures.

The ability to control mineral temperature during X-ray diffraction extends the capability of structural and textural investigations into stability fields not attainable in the ambient laboratory environment. This cold stage was designed for versatility and ease of X-ray access using theta-theta geometry, with applications that can extend to many geological and planetary settings, including cryogenic temperatures.

Acknowledgements: We thank M. Battler for samples. Funding is from NSERC and Western's Centre for Advanced Materials and Biomaterials Research.

References: [1] Battler M. M. et al. (2012) *Icarus*, doi: 10.1016/j.icarus.2012.08.031. [2] Flatt R. J. (2002) *J. Cryst. Growth*, 242, 435–454. [3] Flemming R. L. (2007) *Can. J. Earth Sci*., 44, 1333-1346.

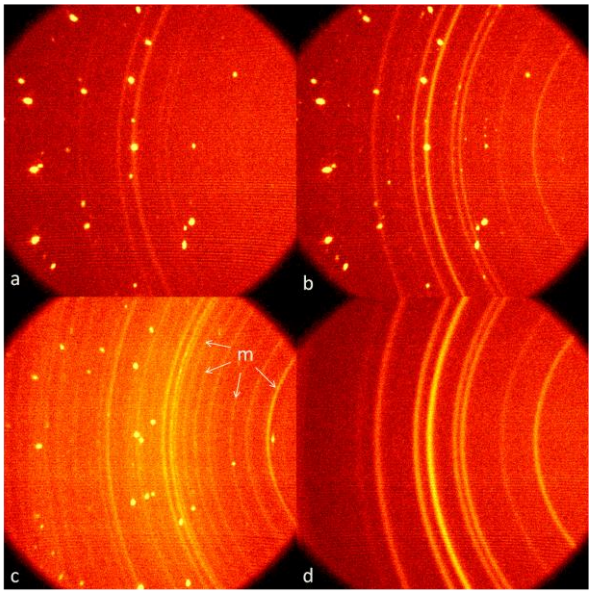

Figure 2: GADDS images from the demonstration experiment taken a) immediately, b) after ~2 hours at –25 °C, c) at 5 °C with secondary mirabilite (m), and d) after equilibration to ambient conditions. The diffraction spots in a and b match the structure of mirabilite, and the Debye rings in a, b, and d match thenardite.