

CONTROLLED ENVIRONMENT CHAMBER FOR SYNTHESIS, SPECTROSCOPY, AND X-RAY DIFFRACTION OF ENVIRONMENTALLY SENSITIVE SAMPLES: A NASA INVESTIGATOR FACILITY AT STONY BROOK UNIVERSITY. A. D. Rogers¹, L. Ehm¹, J. B. Parise¹, and E. C. Sklute², ¹Stony Brook University, Dept. of Geoscience, 255 ESS Building, Stony Brook, NY, 11794-2100, deanne.rogers@stonybrook.edu, ²Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719

Introduction: The low atmospheric pressure and cold temperatures characteristic of the Martian surface creates a set of conditions that facilitates stability or meta-stability for phases that may be deliquescent under terrestrial ambient conditions. Phases that are particularly sensitive to relative humidity (RH), in many cases, cannot be exposed to ambient conditions for more than a few minutes without undergoing deliquescence or phase change. Thus successful analysis of RH/temperature-sensitive samples requires the ability to control and vary RH and temperature (T) during synthesis and characterization. With funding from the NASA Planetary Major Equipment program, we have acquired and installed a Controlled Environment Chamber (CEC) at Stony Brook University that permits measurement of X-ray diffraction patterns, Raman spectra, and VNIR spectra of RH/T-sensitive samples. The chamber (**Figure 1**) consists of a temperature and humidity controlled glove box that contains a benchtop X-ray diffractometer (XRD), portable Raman spectrometer, bell jar, and a VNIR reflectance spectrometer probe/lightsource.

A distinguishing aspect of the CEC, compared to other RH/T-controlled setups (such as Linkam cells attached to Raman/XRD), is that it enables VNIR, Raman, XRD measurements, and visual documentation to all be acquired from the same samples, without concern of any transformation during transfer between instruments. The complementary measurements will provide a unique, robust spectral library for comparison to extant and upcoming data sets.

The CEC is currently being used primarily to investigate RH-induced phase changes in salt systems, salt deliquescence, and amorphous salts (see **Figures 2-3** for example expected data). However, we envision that the CEC could be used for a number of future studies, for example, analysis of experimental fumarolic vapor deposits / alteration products, basalt weathering experiments and characterization under Martian conditions, studies of ice/salt or ice/silicate mixtures, or follow-on studies related to amorphous salts. Given that there are multiple potential applications for such a system, the CEC has been set up as a NASA Investigator Facility Instrument.

Chamber description and capabilities: The glovebox, custom-built by Electro-Tech Systems, Inc. (ETS), has an interior footprint of 24 x 36 inches, three glove ports, and antechamber for loading samples and

equipment. It has a temperature control range of -30°C to 50°C, and can simultaneously control RH down to <3%. It utilizes liquid nitrogen for cooling and dry nitrogen for humidity control. Fogging/frosting on the clear exterior is avoided by circulating dry nitrogen through double-walled acrylic. Humidity can also be controlled through a purge gas generator under ambient temperature conditions, for longer-term experiments that make switching out nitrogen dewars impractical. A 4-cm wide exterior port permits pass-through of fiber optical cables and vacuum tubes as necessary.

Instrumentation: The glovebox can be used to house a portable XRD, Raman and VNIR spectrometer as needed, as well as a bell jar for vacuum-dehydration experiments.

The benchtop XRD unit is an Olympus BTX-2 benchtop XRF/XRD Analyzer with a 30 kV Co anode micro-focus X-ray tube coupled with a high resolution Peltier-cooled CCD detector. The choice of the cobalt tube (as opposed to copper) was based on the need for minimizing fluorescent X-rays from Fe-bearing samples. The measurement range is 5-55° 2 θ with a resolution of 0.25° 2 θ FWHM. The unit is controlled from a computer through wireless connectivity. The BTX has a temperature operating range of -10 to 35 °C and RH range of 0-85%. XRD measurements within the CEC will allow for robust characterization of synthesized materials under the conditions in which they are formed. XRD patterns can be used to verify the amorphous and/or crystalline nature of solid materials, and will be used to document the positions and shapes of intensity maxima, for direct comparison to Mars Science Laboratory CheMin data.

Spectral measurements can be used to track transformations with RH-temperature conditions, and to extend existing spectral libraries. Raman measurements can be made with a B&W Tek iRamanPlus portable Raman spectrometer and 532nm excitation laser. The iRamanPlus has a thermoelectrically cooled detector, and a rugged, industrial grade immersive probe for measurement of irregular surfaces, powders, gels and liquids. The unit is controlled from a computer through wireless connectivity. The iRamanPlus has a temperature operating range of -10 to 60 °C and RH range of 10-85%. VNIR bidirectional reflectance measurements can be made with an ASD Fieldspec3 Max UV-VIS-NIR spectrometer (not purchased with PME funds), which operates from 0.35-2.5 μm . This instrument can

be equipped with an 8 degree foreoptic lens and separate light source, or with a contact probe that contains its own high intensity light source. These measurements are directly comparable to extant data sets (CRISM, OMEGA, Pancam, MastCam), as well as to upcoming data sets from Mars 2020 (MastCam-Z and SuperCam) and ExoMars 2020.

A bell jar capable of achieving vacuum down to 10^{-3} mbar is also available to be placed inside the chamber for vacuum dehydration experiments.

Availability for use by outside investigators: During 2020, the CEC and associated instrumentation is available for 25% time to NASA-funded investigators. During 2021, it is available at 50% time, and then afterward, for 100% of weekdays. Scheduling will be made on a first-come, first-serve basis; contact Deanne.Rogers@stonybrook.edu to request use.

Acknowledgment: The glovebox, XRD, and Raman spectrometer were purchased with funding from the NASA Planetary Major Equipment program (80NSSC18K0516).

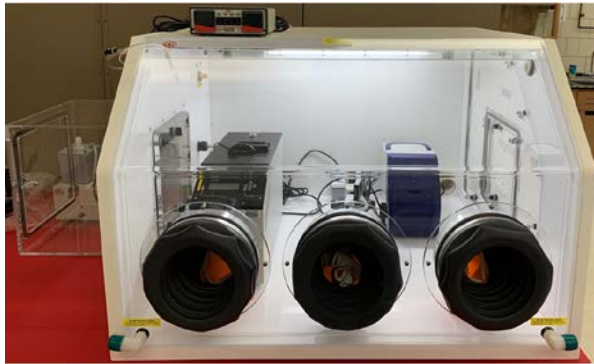


Figure 1. CEC with XRD and Raman instruments.

References: [1] Gregerson et al. (2019), LPSC Abs. 1924.

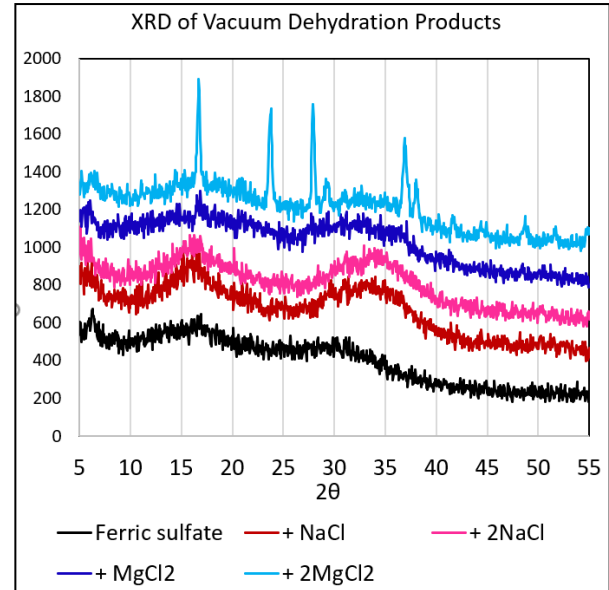


Figure 2. XRD patterns of ferric sulfate and ferric sulfate + chloride brine dehydration products under vacuum. Dehydration products are x-ray amorphous. The patterns in this figure are offset to show detail. From [1].

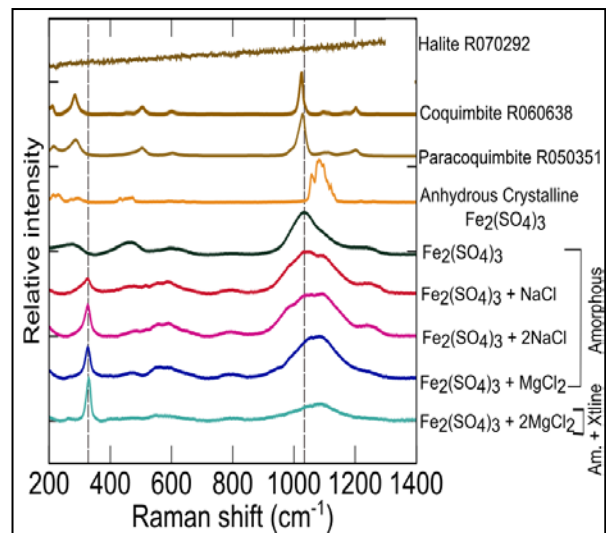


Figure 3. Raman spectra of anhydrous crystalline ferric sulfate and brine dehydration products shown in Fig. 2. Other crystalline ferric sulfates (coquimbite, paracoquimbite) and halite are shown for comparison. Reference samples are from the RRUFF database. Vertical dashed lines are placed at 330 cm^{-1} and 1034 cm^{-1} . From [1].