

EXPERIMENTAL SETUP TO ACQUIRE RAMAN SPECTRA OF MARS-RELEVANT BRINES AND THEIR DESICCATION PRODUCTS AT MARTIAN ATMOSPHERIC PRESSURES AND TEMPERATURES. R. J. Hopkins¹, A. D. Rogers¹, and L. Ehm¹, ¹Department of Geosciences, Stony Brook University, 255 Earth and Space Science Building, Stony Brook, NY 11794. reed.hopkins@stonybrook.edu

Introduction: It has been hypothesized that there may be a relationship between the high weight-percentage of amorphous material found in Martian rocks and soils, and the likely processes of mineral deliquescence and subsequent desiccation of surface/subsurface brines predicted to occur from changes in relative humidity (RH) [e.g., 11, 12, 16, 17]. Amorphous materials represent a significant percentage (~15-70 wt%) of both drilled and scooped sediment samples analyzed by MSL Curiosity at Gale crater [1-6]. Estimates of the composition of the amorphous component in these samples show enrichment in sulfate and iron oxide [7], as well as the possibility of mixed cation sulfate, phosphate, and chloride-perchlorate-chlorate amorphous salts [8]. Chlorides have been found at the Phoenix landing site [9], as well as distributed globally on Mars [10].

Both chlorides and ferric sulfates are known to deliquesce at a high RH, and rapid dehydration of these materials can lead to the formation of an amorphous solid [11,12]. The RH in the subsurface of Mars can go through large variations on both a diurnal and seasonal cycle, which may be favorable to subsurface brine formation [13-15]. Due to the possibility of both ferric sulfate and chlorides contributing to a Martian subsurface brine through deliquescence, it is important to consider mixtures of these brines, and the formation and nature of their potentially amorphous products after rapid dehydration. To help understand these multicomponent brines and their desiccation products, we have put together an experimental setup to hold samples at Martian atmospheric pressures and temperatures, so that they may be spectrally analyzed at these pressures and temperatures. This abstract demonstrates our experimental setup using an example mixture of ferric sulfate and magnesium chloride that has deliquesced into a brine.

Experimental Setup: To prepare the test brine mixture, dry powders of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were mixed in a 1:1 molar ratio. The total starting dry mass was 1.5g. This mixture was placed in a small airtight container that was buffered to 92% RH using DI water. The container was left at room temperature and ambient pressure until the sample was fully deliquesced into a saturated brine.

The sample was analyzed inside a THMS350V temperature-controlled vacuum stage made by Linkam Scientific Instruments. This stage is connected to a

Linkam T95-LinkPad System Controller, which acts as the hub for the system components. A Pfeiffer Vacuum TPR 280 Pirani gauge reads the pressure from inside the stage to the T95 controller. An Edwards 1.5L rotary vacuum pump is used to bring the stage under vacuum. Attached to the vacuum pump is a MV196 motorized vacuum valve, which is controlled by the T95 and sets the pressure inside the stage to between 10^3 and 10^{-3} mbar. A Linkam LNP95 liquid nitrogen pump system is also connected to the stage and T95, and can cool the sample down to -196°C . Both the temperature and pressure inside the stage are manually set using the T95 controller.



Figure 1. The fully assembled setup used in this study.

The THMS350V stage has a 0.3 mm thick glass window above the sample holder. Through this window, the sample can be analyzed with a variety of spectroscopic techniques, or the stage can be placed under a microscope. Our setup is currently assembled with a B&W Tek i-Raman Plus Raman spectrometer utilizing a 532 nm laser.

Using a pipette, 300 μL of the 1:1 $\text{Fe}_2(\text{SO}_4)_3$ and MgCl_2 brine mixture was put in a quartz sample cup, which was positioned on the cooling platform inside the THMS350V stage. Slowly over about 5 minutes, the temperature and pressure inside the stage were simultaneously dropped to $-23 \pm 2^\circ\text{C}$ and 5 ± 0.75 mbar, respectively. Once the stage reached the desired temperature and pressure, an initial Raman spectrum was taken, shown as spectrum 0:13 in Figure 2. Over the next ~7 hours, spectra were acquired every 45-60 minutes.

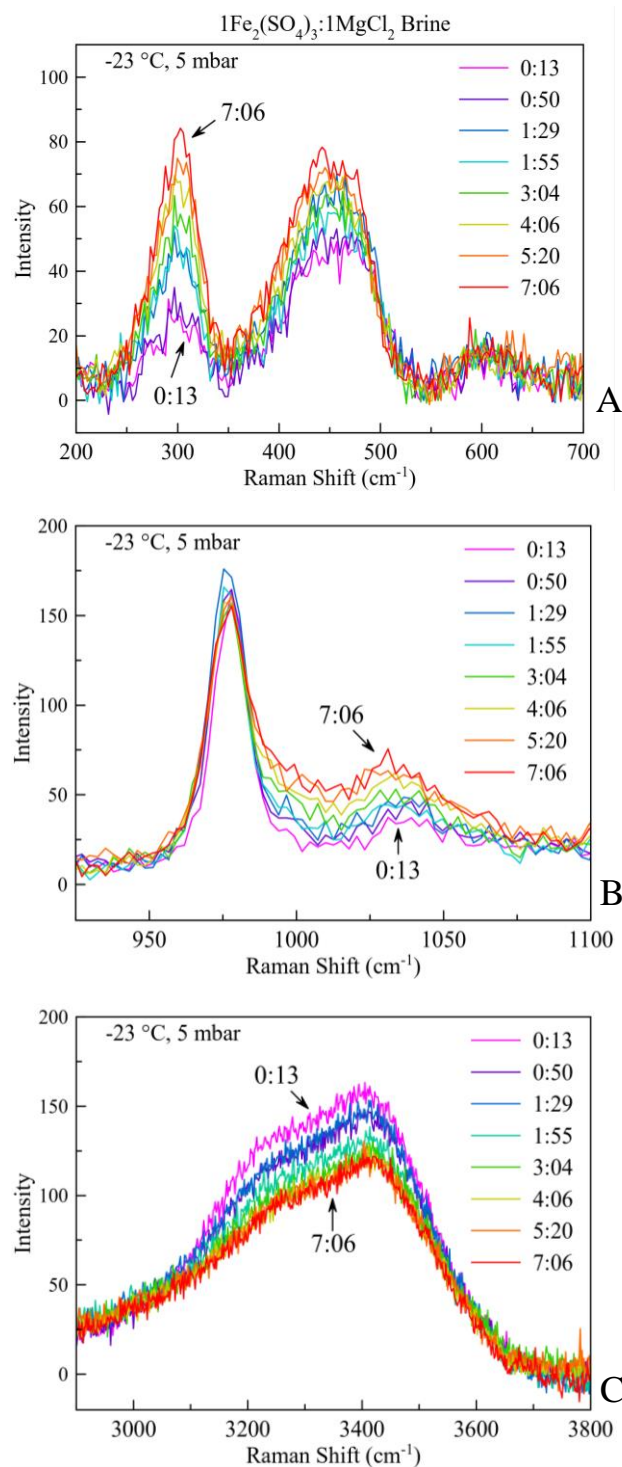


Figure 2. Raman spectra of the 1Fe₂(SO₄)₃:1MgCl₂ brine mixture over time inside the THMS350V stage between the start of the experiment and ~7 hours. Spectra are averages of 50, 10 second integrations. All spectra are baseline corrected with the same rubberband parameters.

Discussion: During the ~7 hours in the stage, the Fe₂(SO₄)₃ and MgCl₂ brine did not initially freeze, but did increase in viscosity over time, and may have formed into a solid during the ~7 hours. While no precipitation was observed, changes over time in the intensities of spectral features show that dehydration occurred (Fig. 1A-C). The intensity of the broad O-H bands from ~3100-3600 (Fig. 1C) dropped over the ~7 hours the sample was in the stage, indicating loss of water over time. As the sample dehydrated, the concentration of iron sulfate species increased, causing the intensities of the Fe-O and SO₄²⁻ features shown in Figures 1A and 1B to increase over time.

We were successful in taking spectra of a multicomponent brine at a Mars-relevant temperature and pressure, and we observed a physical change in the brine over time using Raman spectroscopy. In our planned future studies, we will refine this setup and our procedures to acquire better spectra. We plan on taking spectra of many different multicomponent brines of varying compositions and molar ratios, as well as testing how the brines respond to the range of Mars-relevant temperatures and pressures possible with this setup. Additionally, we hope to use this setup to determine the deliquescence RH for various salts at Mars-relevant temperatures.

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