OBSERVATION OF DEHYDRATION-INDUCED PHASE CHANGES IN MARS-RELEVANT SALTS.
B. A. Howl, A. D. Rogers, L. Ehm, Dept. of Geosciences, Stony Brook University (bryan.howl@stonybrook.edu)

Introduction: X-Ray Diffraction (XRD) patterns acquired by the Mars Science Laboratory (MSL) CheMin instrument indicate a significant proportion of amorphous material (~20-30 wt%) in Martian soils [1]. Evolved Gas Analyses [2] suggests that the majority of evolved volatiles (H₂O, SO₂, Cl) is bound within amorphous phases (structural and/or adsorbed), and APXS measurements indicate the presence of CI-bearing species that were not detected in the crystalline fraction by CheMin [3]. Mass-balance calculations based on measurements by the APXS and SAM instruments have constrained the bulk chemistry of the amorphous component [4]. However, the individual phases present in the amorphous component are not as well constrained.

An important step in resolving this problem is to understand what salt species are likely to amorphize under current Martian conditions. Previous laboratory studies have shown that amorphous salts can form through two pathways – via rapid dehydration of concentrated brines or rapid dehydration of crystalline hydrated salts. For example, crystalline ferric sulfates or mixed-component salts deliquesce to brine solutions under high relative humidity (RH) conditions in laboratory studies. These solutions then dehydrate to form amorphous phases under vacuum or in a low RH buffer environment [5,6,7]. Some hydrous crystalline sulfate phases have also been shown to dehydrate under vacuum to an amorphous phase [e.g. 8]. These amorphization pathways are relevant to Mars, as diurnal and seasonal RH variations could facilitate similar reactions on the surface or near-subsurface. This investigation builds on previous work that examined the amorphization pathways of Fe and Mg sulfates [e.g. 5-10], by extending to other Mars-relevant salts. In this presentation, we report on the phase changes of Ca-chloride, Mg-chloride, Fe(II)-chloride, and K-Al-sulfate under various amorphization pathways in order to identify new candidate phases for the amorphous component of soils on Mars.

Methods: This study investigates the effect of 3 reaction pathways on 4 salt systems. The pathways are:

1) Vacuum dehydration of hydrous mineral phases.
2a) Vacuum dehydration of a brine solution formed via deliquescent of salt with a high-RH buffer (deionized [DI] H₂O). 2b) Dehydration of the same brine solution with a low-RH buffer (LiCl). The chemical formulas for the hydrated salts used for starting materials (SM) in each pathway are: KAl(SO₄)₂·12H₂O, CaCl₂·6H₂O, MgCl₂·6H₂O, Fe(II)Cl₂·4H₂O.

For vacuum experiments (1,2a), an Applied Vacuum Engineering BJ-8-VF borosilicate bell jar and Edwards rotary vane vacuum pump that achieves pressures down to 10⁻³ mbar was used. Approximately 1g of each salt was placed into a vial, and the vials were placed in the vacuum chamber for 4 days.

Deliquescent of salts (2a,b) was performed by placing roughly 1g of starting material into a weigh boat atop a plastic stand. The stand was then placed in an air-tight plastic container filled partially with DI water to maintain an environment of approximately 92% RH. After 6 days, the resultant brines were each split approximately in half and transferred to another container for dehydration via vacuum or LiCl buffer. One salt, KAl(SO₄)₂, did not deliquesce, but to enable the following experiments was mixed into a roughly saturated solution in DI water at room temperature.

Vacuum dehydration of brines (2a) was performed for the resultant brines via the same procedure as for the hydrated solids. Brines were placed under vacuum for 48 hours. Dehydration of brines via buffer solution (2b) was performed using the same containers, weigh boat, and stands as were used for deliquescent, except the buffer solution used was LiCl+DI to maintain a RH of ~11%. Brines were kept in the buffered environment for 8 days.

XRD patterns were acquired using a Rigaku MiniFlex with a Cu Ka radiation source, with detector setting optimized to reduce the fluorescence of iron-bearing samples, and a quartz zero-background sample holder. For SM and products of 1, 2b, patterns were acquired over a 2θ range of 15-90°. Due to operator error, the 2θ range for products of 2a is only 15-70°.

Results: Of the experiments performed here, the only material to form a fully amorphous phase is the potassium aluminum sulfate, which amorphizes under pathways 1 and 2a. Pathway 2b produces a distinctly different XRD pattern with an elevated background indicating a phase change and possibly the formation of some amorphous material.

CaCl₂ products produce similar XRD patterns under pathways 1 and 2a which are distinct from the SM in that peak positions are not the same, and the background signal of the products is much higher than the SM, possibly indicating a mixture of crystalline and amorphous products. All peaks in the 2θ region 40-70° of pattern 1 match closely with peaks in the same region of 2a. However, two peaks that appear at ~31 and 34° in 1 are not present in 2a. This could indicate a mixture of phases, one of which is present in 1 but absent from 2a. The pattern of 2b is unusable because the sample deliquesced to a brine inside of the XRD instrument.
The change in XRD patterns of MgCl$_2$ behaves similarly to that in the CaCl$_2$ experiments. Products 1 and 2a have different peak location from SM, along with an elevated background, again potentially indicating some amorphous product mixed with crystalline. Again, 1 and 2a share some peak locations, with some differences between 30–40°.

FeCl$_2$ forms different crystalline phases under pathways 1, 2a that are both distinct from SM. 2b produces a pattern with very low peaks relative to background, indicating a poorly crystalline product. FeCl$_2$ also did not fully deliquesce, so the brine solution for experiments 2a,b had to be vacuum filtered from the latent solid. The solid seemed visually to be distinct in color and texture from the starting material, but not enough was recovered to perform XRD analysis.

Discussion: Of the materials studied here, potassium aluminum sulfate is the most likely to amorphize under Martian conditions. From its demonstrated propensity for amorphization under vacuum, it is clear that low-pressure phase transitions exist that have yet to be documented. Further investigation to determine whether this salt is stable or metastable under modern Martian conditions may be warranted.

K, Al have not been shown to constitute a large proportion of the amorphous component of soils [4]. However, these have been shown to be products of basaltic acid weathering [11,12]. KAl(SO$_4$)$_2$ was also shown here to not deliquesce at high RH, and to not become amorphous via brine dehydration except under vacuum. RH-driven dehydration is the amorphization pathway most relevant to the Martian surface, but even though it was not observed in these experiments, this transition may be possible if an RH-dehydration experiment were to be conducted under Martian ambient pressure. Finally, our data suggest that the chloride samples may have partially amorphized, but this will be further evaluated through longer-term experiments as well as via Raman spectroscopy.

Acknowledgements: This work was supported by the NASA SSW program (80NSSC18K0535) and PME program (80NSSC18K0516).


Figure 1: XRD patterns of starting material (blue), product of pathways 1 (red), 2a (green), 2b (orange), offset.