

SEQUESTRATION OF MIXED SALTS IN THE AMORPHOUS SOIL FRACTION ON MARS. A. D. Rogers¹, J. Gregerson¹, E. C. Sklute², M. Rucks¹, H. B. Jensen, R. J. Reeder¹, and M. D. Dyar², ¹Stony Brook University, Geosciences Dept. 255 ESS Building, Stony Brook, NY. 11794-2100, Deanne.Rogers@stonybrook.edu. ²Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075.

Introduction: It has been repeatedly demonstrated that hydrated ferric sulfates deliquesce under high relative humidity (RH) conditions (>90%), and that upon rapid exposure to lower RH conditions they will re-precipitate into an amorphous phase [1-3]. If ferric sulfates are present in Martian soils, they have the potential to form brines at the grain scale under conditions of high RH [3], which can occur in certain locations and times of day [4-6]. Just as H₂O frost/ice can undergo sublimation with increasing temperature, hydrated sulfates that are sensitive to RH could also undergo phase changes or deliquescence with changing temperature (and thus RH). Once RH conditions were lowered, an amorphous phase could form. Thus amorphous sulfates could be present in Martian soils, formed either from deliquesced ferric sulfate crystals, or from direct precipitation from a free-flowing surface or subsurface brine. Once the amorphous phase forms, it can persist for years under low RH conditions. Even when exposed to higher RH conditions, it is slow to convert to a crystalline form [2].

It remains uncertain, however, how the presence of other ions in ferric sulfate brines would affect the end product of RH fluctuations or brine evaporation. If these amorphous phases are forming on Mars, it is unlikely that they form from pure ferric sulfate brines. To that end, we have investigated the addition of chlorides and carbonates to ferric sulfate brines to understand 1) the changes in crystallinity and stability and 2) the visible and infrared spectral properties of the precipitate.

Methods: Salts of Fe₂(SO₄)₃, FeCl₃, MgCl₂, and CaCl₂ were deliquesced in 90% relative humidity to make saturated solutions. Saturated solutions of NaHCO₃ were made through the addition of salt to water with stirring. Binary and ternary mixtures (**Table 1**) of the saturated solutions were then rapidly dehydrated by desiccation in low RH chambers (LiCl buffering salt at 25 °C; 11% RH) to simulate rapid evaporation, or by vacuum (10⁻³ mbar) to simulate low pressure boiling.

End products were simultaneously analyzed by XRD (Rigaku Ultima-IV; Cu-K α) and mid-infrared (MIR) attenuated total reflectance (ATR) spectroscopy on a Thermo Fisher Nicolet 6700 FTIR, 256 scans per spectrum, or visible near infrared (VNIR) spectroscopy on an ASD Fieldspec Max3 ($i=30$, $e=0$).

Results: Compositions, along with physical and

spectral attributes, of the end products are summarized in **Table 1**, VNIR spectra are shown in **Figure 1** and MIR ATR spectra are shown in **Figure 2**.

Table 1. Brine mixture dehydration products analyzed in this study along with physical and XRD attributes. Crystalline phases are listed if they are the sole phase in the XRD pattern. Ratios indicate vol-vol mixing of saturated solutions. Solid indicates a sample that grinds into a powder.

Brine	11% RH	XRD	Vac	XRD
CaCl ₂	liquid	-	solid	cryst
FeCl ₃	liquid	-	solid	amorph
MgCl ₂	liquid	-	solid	bischofite
1CaCl ₂ :2Fe ₂ (SO ₄) ₃	solid	gypsum	solid	gypsum
1FeCl ₃ :2Fe ₂ (SO ₄) ₃	gel	-	solid	amorph
1MgCl ₂ :2Fe ₂ (SO ₄) ₃	gel	-	solid	amorph
1NaHCO ₃ :1Fe ₂ (SO ₄) ₃	solid	amorph	solid	amorph
1FeCl ₃ :1NaHCO ₃ : 2Fe ₂ (SO ₄) ₃	solid	amorph	solid	amorph
1MgCl ₂ :2NaHCO ₃ : 2Fe ₂ (SO ₄) ₃	solid	amorph	solid	amorph

Brines with NaHCO₃. Addition of bicarbonate leads to rapid bubbling, likely due to rapid loss of CO₂ as a gas from the highly concentrated chloride and/or sulfate brine (salting out), leaving the bicarbonate's sodium in solution. Interestingly, these brines solidify more readily than pure sulfate or sulfate/chloride brines and the solid X-ray amorphous products are more stable than those that did not interact with NaHCO₃. The NaHCO₃/Fe₂(SO₄)₃ combination has a different XRD baseline slope than the other combinations, which may prove useful in the identification of such products. In the NIR, spectral features of the amorphous products are similar to those of ferric sulfate, with one sample (2FS:1MgCl:2BC) showing slightly deeper hydration features. The addition of MgCl₂ causes the spectral maximum at ~1.1 μ m to narrow and move to higher wavelengths (~1.3 μ m). Towards the visible range, the amorphous mixtures are very different from pure amorphous ferric sulfate, with a major reflectance minimum near 0.84 μ m.

Brines with Chlorides. The hygroscopic chlorides will not solidify at 11% RH. When mixed with Fe₂(SO₄)₃, the 11% RH samples partially solidify with

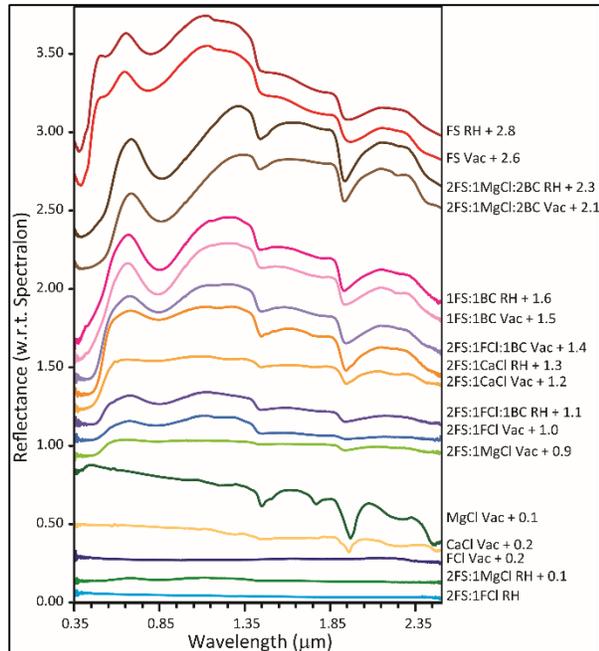


Figure 1. VNIR spectra of salt mixtures. Numbers indicate volume ratios of saturated fluids. Abbreviations are ferric sulfate (FS), ferric chloride (FeCl), magnesium chloride (MgCl), calcium chloride (CaCl), sodium bicarbonate (BC). Spectra are offset by indicated amount.

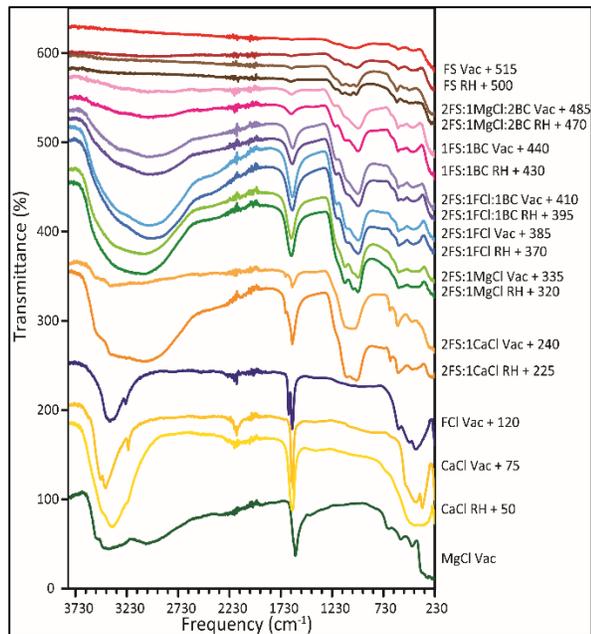


Figure 2. MIR ATR spectra of salt mixtures. Numbers indicate volume ratios of saturated fluids. Abbreviations are ferric sulfate (FS), ferric chloride (FeCl), magnesium chloride (MgCl), calcium chloride (CaCl), sodium bicarbonate (BC). Spectra are offset by indicated amount.

Mg<Fe<Ca % solid at 11% RH. The $\text{Fe}_2(\text{SO}_4)_3/\text{CaCl}_2$ mixture was the only one stable enough for XRD under ambient atmospheric conditions (15-21% RH) and only

displayed peaks for gypsum with no trace of an Fe-bearing phase or chloride in the XRD pattern. All chloride samples solidified under vacuum. Though the $\text{Fe}_2(\text{SO}_4)_3/\text{CaCl}_2$ mixture was again an XRD match to gypsum, the $\text{Fe}_2(\text{SO}_4)_3/\text{MgCl}_2$ and $\text{Fe}_2(\text{SO}_4)_3/\text{FeCl}_3$ mixtures were X-ray amorphous, indicating that MgCl_2 and FeCl_3 could potentially hide in the amorphous fraction. Importantly, these amorphous sulfate-chloride mixtures are nearly featureless in the NIR range, similar to crystalline NaCl salts and chloride-bearing units detected on Mars [7].

Conclusions and implication: Two mixing scenarios can easily be theorized from these findings. The first is that hygroscopic ferric, magnesium, or calcium chlorides could lead to the local dissolution of sulfates and the resultant mixture could then become an amorphous solid when RH or pressure conditions favored solidification. The second is that acidic brines (either free-flowing or at the grain scale) could dissolve carbonates, liberating CO_2 but incorporating the cations, and the resultant brine could then precipitate an amorphous solid.

Brines that result from mixtures of salts with ferric sulfate form X-ray amorphous solids that can be more (sodium bearing) or less (Fe-, Ca-, or Mg-chloride bearing) stable with respect to RH than pure ferric sulfate amorphous solids. One could imagine that a range of brine and solid stabilities could be achieved through the mixing of various salts. More work is needed to understand what chemical components could be hiding in the amorphous fraction [11] of Martian soils.

Lastly, the VNIR and MIR ATR spectra of these mixtures do not often reveal the contents of the mixture. For example, amorphous sulfate-chloride mixtures are nearly featureless in the NIR. Chloride-bearing units are commonly observed on Mars [8]. Spectrally, they are consistent with pure NaCl-basalt mixtures, with little evidence for other salts present [9]. However, the absence of other salts is difficult to reconcile with an evaporation scenario. Could the spectral properties be consistent with amorphous salt mixtures? More work is needed to constrain the compositions and spectral characteristics of the amorphous salt mixtures that could be present on Mars.

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