

### PHASE TRANSITIONS OF AMORPHOUS IRON(III) SULFATES AT AN INTERMEDIATE HUMIDITY

J. Gregerson<sup>1</sup>, A. D. Rogers<sup>1</sup>, E. C. Sklute<sup>2</sup>, R. J. Reeder<sup>1</sup>, and M. D. Dyar<sup>2</sup>, <sup>1</sup>Stony Brook University, Geosciences Dept. 255 ESS Building, Stony Brook, NY. 11794-2100. <sup>2</sup>Mount Holyoke College, Dept. of Astronomy, South Hadley, MA, 01075.

**Introduction:** There is an abundance of data suggesting the presence of amorphous phase(s) of hydrated iron(III) sulfate on the surface and shallow sub-surface of Mars:

- The CheMin X-ray diffractometer instrument on Curiosity has detected a significant (~30 wt%) amorphous, likely multi-phase component in Martian soils that is hydrated and contains abundant Fe and S [2]. Using chemical constraints, amorphous sulfate could comprise up to ~9 wt% of Martian soils [3].

- Laboratory experiments have shown that ferric iron sulfate can form an amorphous solid phase via dehydration of a concentrated aqueous brine (formed from deliquescence of crystalline ferric sulfate) and stay amorphous among Mars-relevant conditions [3,6].

- These amorphous solids can increase hydration state upon exposure to increased relative humidity (RH) while remaining amorphous, and are slow to convert to crystalline form [4].

- Preliminary experiments [5] show that the substitution of other elements in the amorphous solid can have a significant effect on the stability and persistence of this amorphous phase. However, the underlying cause for this (hydration state, ion chemistry) was not determined.

Amorphous ferric sulfates could be important components of Martian soils or planetary fumarolic deposits, yet there are still major open questions about how these amorphous ferric sulfates change over time when subject to humidity or atmospheric pressure changes.

Ferric sulfate is known to remain amorphous at RH=11%, but will deliquesce to a brine at higher RH levels (>75%RH) [3,6]. Amorphous ferric sulfate has been documented to remain amorphous over short periods of time at 33% RH [4], but its behavior at such

an extended period of time and phase changes were observed.

**Methods:** A saturated solution of  $\text{Fe}_2(\text{SO}_4)_3$  was prepared by deliquescing anhydrous solid iron(III) sulfate in high RH.  $\text{Fe}_2(\text{SO}_4)_3$  solutions were then rapidly dehydrated by both desiccation in low RH chambers (LiCl buffering salt at 25 °C; 11% RH) to emulate rapid evaporation, or by vacuum ( $10^{-3}$  mbar) to emulate low pressure boiling, as per a previous study [3]. These dehydrated solid samples were then transferred to 33% RH chambers ( $\text{MgCl}_2$  buffering salt at 25 °C) and observed over a period of 9 weeks (63 days). Samples were weighed to measure changes in mass due to varying water content. Any solid phases remaining were separated and phase-identified using X-ray Diffraction (XRD).

**Results:** Exposure to 33% RH conditions had a similar effect on both samples of amorphous ferric sulfate (one formed from a humidity-controlled desiccated brine and one formed from a vacuum-dehydrated brine). Both samples of amorphous  $\text{Fe}_2(\text{SO}_4)_3$  underwent the same phase transitions, but did so through variable time scales. **Table 1** shows the time periods that each sample was observed to be in a certain phase after introduction to 33%RH. Crystalline phases observed in both samples were nearly identical and XRD analysis determined that these were a mixed-phase system containing rhomboclase and kornelite.

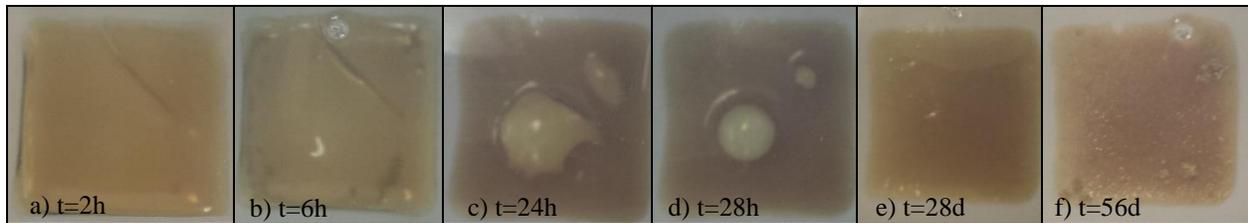
*RH-Desiccated  $\text{Fe}_2(\text{SO}_4)_3$ :* This sample was dehydrated in a 11% RH chamber before being transferred to the 33% RH chamber. The initial amorphous phase began to swell and deform over the first few hours, and a liquid was first seen after 4 hours indicating the sample was beginning to deliquesce (**Fig. 1a, 1b**). After 24 hours the liquid dominated the system (**Fig. 1c**), and after 26 hours the amorphous phase had

$\text{Fe}_2(\text{SO}_4)_3$ Sample:	Initial Amorphous Phase:	Aqueous Solution:	Crystalline Phases:	Final Amorphous Phase:
RH-Desiccated	0-26hours	4hours-28days	39days-end	28days-end
Vacuum-Dehydrated	0-4days	2hours-24days	24days-end	24days-end

**Table 1.** Each phase observed during rehydration of both amorphous  $\text{Fe}_2(\text{SO}_4)_3$  samples as well as the first and last time such phase was observed after the sample was introduced to 33%RH.

an intermediate humidity over extended periods of time (>3days) has not been intricately documented. Therefore, a suite of samples containing amorphous ferric sulfate were subjected to 33% RH conditions for

been completely deliquesced and only a solution remained (**Fig. 1d**). After 28 days in 33%RH, the



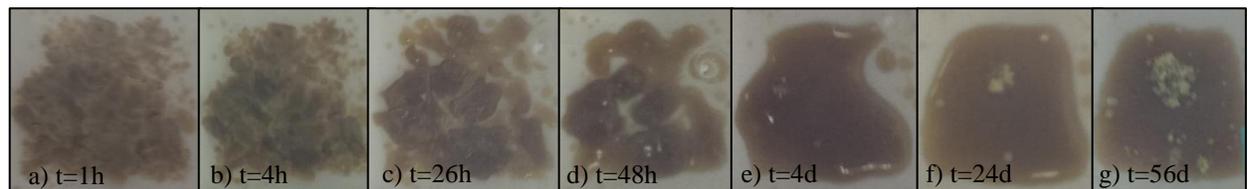
**Figure 1.** Photos of the RH-Desiccated  $\text{Fe}_2(\text{SO}_4)_3$  sample at various times after introduction to 33%RH. **1a)** Relatively unchanged amorphous solid after 2h. **1b)** Amorphous solid beginning to deform and deliquesce after 6h. **1c)** Sample almost completely deliquesced after 24h. **1d)** Uniform liquid brine after 28h. **1e)** Solution begins to form a new amorphous phase after 28d. **1f)** Crystals embedded in amorphous solid after 56d.

sample (now liquid) began to dehydrate to form a new amorphous phase (**Fig. 1e**). Crystals began forming within the amorphous solid after 39 days and continued to grow until the end of the experiment (**Fig. 1f**).

*Vacuum-Dehydrated  $\text{Fe}_2(\text{SO}_4)_3$ :* This sample was dehydrated at low pressure before being transferred to the 33% RH chamber. The behavior of this sample under such humidity is similar to that of the RH-dehydrated sample, but with a few key differences (**Fig. 2a-g**). The vacuum-dehydrated amorphous solid remained for four times as long as the RH-desiccated sample under 33% RH. Additionally, crystals (along with the new amorphous phase) formed sooner and

future work will repeat these experiments with RH monitors.

It is currently unknown what similarities are shared between the initial and final amorphous solid phases, however changes in mass suggest that the latter phase has a higher hydration state than the former. It also appears that the method in which the  $\text{Fe}_2(\text{SO}_4)_3$  brine is dehydrated to form an amorphous solid has an effect on the resistance of the solid to changes in humidity and the rate at which deliquescence occurs. The original dehydration method does not appear to affect which crystalline phases are formed, however, as both samples produce a mixture of rhomboclase and kornelite.



**Figure 2.** Photos of the Vacuum-Dehydrated  $\text{Fe}_2(\text{SO}_4)_3$  sample at various times after introduction to 33%RH. **1a)** Relatively unchanged amorphous solid after 1h. **1b)** Amorphous solid beginning to deliquesce after 4h. **1c)** Sample partially deliquesced after 26h. **1d)** Sample mostly deliquesced after 48h. **1e)** Uniform liquid brine after 4d. **1f)** Crystals begin to form after 24d. **1g)** Crystals embedded in amorphous solid after 56d.

grew larger in the vacuum-dehydrated sample.

**Discussion and Conclusions:** Although it has been shown that amorphous ferric sulfates can remain amorphous at 33%RH for short periods of time [4], sustained exposure to this amount of humidity resulted in the following pathway of phase transitions for hydrated amorphous ferric sulfate:

**Amorphous** → **Amorphous + Liquid** →  
**Liquid** → **Amorphous** → **Amorphous + Crystalline Phases**

This final set of phases could be subject to further alterations after the observed 9-week period. The second formation of an amorphous phase suggests the possibility that RH conditions were not maintained;

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