

FERRIC SULFATES ON MARS: MISSION OBSERVATIONS AND LABORATORY INVESTIGATIONS.

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Fe-sulfates on Mars: Sulfate is one of the major types of secondary minerals found on Mars by recent missions, which reinforced its importance for Mars science. Sulfates are excellent hosts of water, the sinks of acidity, and maybe the most active species in the past and current surface/near-surface processes on Mars [1]. Although Mg- and Ca-sulfates were identified with wide vertical and horizontal spread in Valley Marineris, Meridiani Planum, and at North Polar Region [2,3,4,5], Fe-sulfates have rarely been observed from orbiters. A few occurrences were recently reported by CRISM team [6], but the overall quantity of Fe-sulfates at the potential occurrences is not comparable with those of Mg-sulfates.

Ferric sulfates were found at both landing sites of Mars Exploration Rovers. Jarosite takes ~10 wt% of Meridiani Planum outcrop at Opportunity exploration site [7]. A non-specific ferric sulfate was indicated in the excavated salty soils by Mössbauer spectrometer (MB) [8], for which additional spectral analysis of one site (Paso Robles), using Pancam, MiniTES data, laboratory results, suggests that ferricopiapite should be the major constituent [9]. A two-layer salty soil was excavated by Spirit rover at Tyrone site [10]. APXS data of upper-layer soil (whitish) suggests a Ca ~ SO₃ correlation and an elevated Fe content [11]. No APXS and MB measurements were made on the lower-layer (yellowish) soil. A Pancam spectral analysis [12] suggests that ferricopiapite is the major contributor to the yellowish Tyrone soil spectrum, together with jarosite, fibroferrite, rhomboclase, and gypsum.

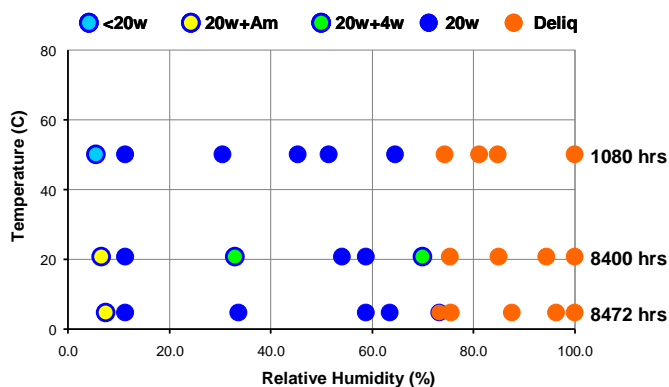
After ~190 sol exposure at the current Mars surface conditions, the Pancam L2/L7 band ratio of yellowish Tyrone soil shows a reduction of > 20%. Preliminary laboratory experiments suggest that dehydration of ferric sulfates (kornelite and copiapite) can be a potential cause; however it only accounts for 7-8% reduction of L2/L7 band ratio [10]. This abstract reports two new hypotheses based on a set of systematic laboratory experiments of ferric sulfates.

Experimental study of ferric sulfates: In laboratory, we synthesized eight ferric sulfates and conducted a systematic spectroscopic study on them, including Raman, XRD, MIR and VIS-NIR, reported last year [13]. As the second step of this Mars Fundamental Research project, 150 hydration/dehydration experiments were conducted on five selected ferric sulfates. Our goal was to establish the stability fields and phase transition pathways of these ferric sulfates. In these

experiments, water activity, temperature, and starting structure are the variables. Acidic, neutral, and basic salts were used, but no redox state change was intended or observed. The five starting phases were ferricopiapite ($\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$), kornelite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$), rhomboclase ($\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), pentahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$), and amorphous pentahydrate. The hydration/dehydration experiments were conducted at three temperatures ($T=50^\circ\text{C}$, 21°C , 5°C). Ten relative humidity (RH) buffers (from 6% to 100%) were used at each T. Thousands of coupled non-invasive Raman and gravimetric measurements were made at regular time intervals on the intermediate products to monitor the phase transitions. These 150 experiments have been running for almost one year, most have reached the equilibrium.

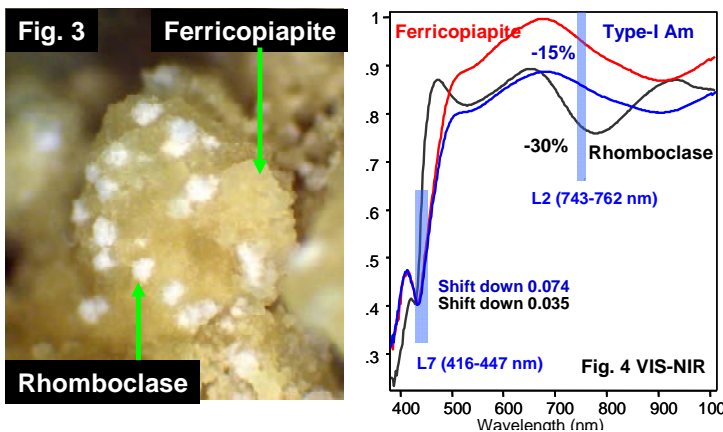
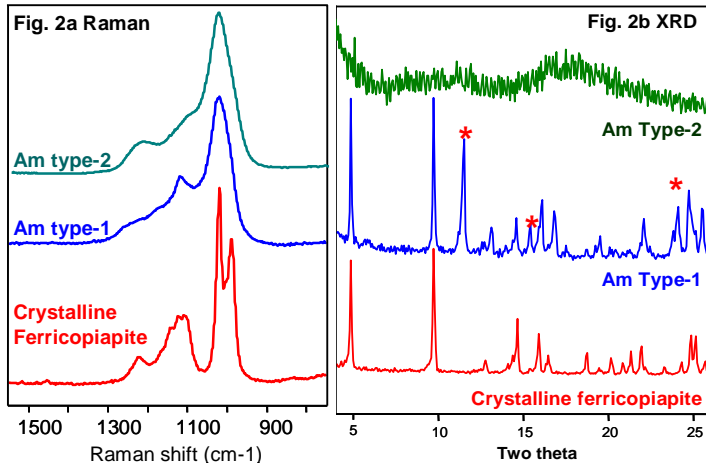
Results and discussion: Among the ferric sulfates that

Figure 1. Dehydration/rehydration of Ferricopiapite $\text{Fe}_{4.67}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$



we investigated, ferricopiapite bears the highest importance (Fig. 1), because (1) it has the highest hydration degree $\text{H}_2\text{O}/\text{SO}_4=4.5$ among ferric sulfates with $\text{Fe}^{3+}:\text{SO}_4=2:3$; (2) it crystallizes from aqueous solutions at a temperature range much wider (from 21°C to -10°C) than that of highly hydrated Mg-sulfates (11w and 7w); (3) it was suggested to be the major constituent of the Gusev salty soils [11,12].

It is remarkable that in these results (Fig.1), unlike the highly hydrated Mg-sulfates that would dehydrate readily at mid-low RH ($\leq 34\%$), ferricopiapite remains unchanged over long period of time under dry conditions (RH~11% at 21°C and 5°C). Because an amorphous Fe-sulfate appeared at lowest RH (7%) after 350 days' dehydration from ferricopiapite, more experiments were conducted to investigate the amorphization process of ferricopiapite.



We found that there are two pathways for amorphization and two different types of amorphous ferric sulfates can be produced (Fig. 2). The first starts with crystalline ferricopiapite, and using either vacuum desiccation (~ 130 m τ at 21 °C) or low RH dehydration ($\leq 7\%$ RH at 50 °C, 21 °C, 5 °C, Fig. 1), only partially amorphized ferric sulfate was formed (Am type-1). One to five structural waters can be lost in this way. The product shows the loss of fine Raman spectral details (Fig. 2a) and a maximum peak upshift of 10 cm $^{-1}$. Its XRD pattern (Fig. 2b) agrees with a partial amorphization. The residual crystalline component has a few additional XRD lines and lineshifts that suggest much modified d spacing from the starting ferricopiapite structure.

The second way of forming amorphous ferric sulfates starts with a Fe $^{3+}$ -S saturated aqueous solution evaporated at a low RH ($\leq 11\%$) and a high T (50 °C & 21 °C). Totally amorphized ferric sulfates were produced (Am type-2), identified by both Raman and XRD. We found that this type of amorphous ferric sulfates can take four to eleven structural waters per [Fe $_2$ (SO $_4$) $_3$] unit. The gradual increase of water content is indicated by Raman peak downshift (Maximum shift ~ 12 cm $^{-1}$).

It has been frequently seen that ferricopiapite partially converts to rhomboclase in the natural precipitations of Fe $^{3+}$ -S aqueous solutions (Fig. 3), and occasionally during the dehydration of ferricopiapite (Fig. 1). This conversion, i.e. from a basic salt to an acidic salt, appears to be influenced by a delicate equilibrium of environmental acidity. It is also an indication of dehydration from H $_2$ O/SO $_4$ =4.5 to H $_2$ O/SO $_4$ =2.0. Notice rhomboclase can be produced from the aqueous solutions with Fe $^{3+}$:SO $_4$ < 2:3. In our experiments, rhomboclase is observed to be extremely stable at mid-low RH ($\leq 59\%$) and in wide T range (50 °C to 5 °C).

Applications to Mars surface observation:

Based on the results of our laboratory experiments, we propose two additional mechanisms that might be responsible for the Pancam L2/L7 band ratio reduction of Tyrone yellowish salty soils after its 190 sols exposure to the current Mars surface conditions. Assuming ferricopiapite is indeed the major constituent of the yellowish salty soil [13], after exposing to extremely low RH ($\sim 0\%$ during daytime), amorphization and the conversion to rhomboclase can both happen, as they happened in our experiments. Figure 4 compares the VIS-NIR spectrum of ferricopiapite with the spectra of type-I amorphous ferric sulfate and that of rhomboclase. A reduction of spectral contrast appeared in the spectrum of type-I Am, and a new absorption band near 750 nm appears in the spectrum of rhomboclase. When converting these spectra to Pancam spectral resolution (blue bars in Fig. 4), these spectral differences would cause 15% and 30% of the L2/L7 band ratio reductions. Based on the experimental results, the potential causes for the spectral change of Tyrone yellowish salty soils are the dehydration of ferric sulfates (copiapite and kornelite), the amorphization of ferricopiapite, and the conversion of ferricopiapite to rhomboclase.

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