

A COMPREHENSIVE SPECTROSCOPIC STUDY (RAMAN, MIR, VIS-NIR, LIBS, XRD) OF SYNTHETIC Fe^{2+} , Fe^{3+} , Mg^{2+} , Al^{3+} COPIAPITES. W. G. Kong^{1,2}, Alian Wang¹, J. J. Freeman¹, P. S. Sobron¹,
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Introduction: Sulfates were found on Mars by spectrometers on orbiters (OMEGA and CRISM) and on two Mars Exploration Rovers (Spirit, Opportunity). Compared with Mg- and Ca-sulfates, there were very few reports on the finding of Fe-sulfates from orbital remote sensing, while Fe^{3+} -sulfates were found on the ground at two rover exploration sites. Jarosite ($\text{K,Na,H}_3\text{O}$) $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ was identified by Mössbauer spectrometer (MB) on Opportunity taking ~10 wt% of Meridiani outcrop [1]. Within the light-toned salty soils exposed by Spirit rover at several different sites (Paso Robles, Dead Sea, and Tyrone) in Columbia Hills at Gusev Crater [2, 3], the MB spectral analysis indicated the existence of a non-specific ferric sulfate [4]. A Pancam spectral deconvolution suggested the existence of ferricopiapite, hydronium jarosite, fibroferrite, rhomboclase and paracoquimbite in these soils [5]. Another study combining the Pancam and MiniTES data from Spirit with laboratory experiments also suggested that ferricopiapite is the major constituent in Paso Robles salty soils [6]. Both of these studies reinforce the importance of copiapite group minerals for the study of martian salts.

Copiapite group minerals are frequently observed in terrestrial acidic drainages. A variety of bivalent and trivalent cations entered the copiapite structure and formed a series of copiapite with different colors. Similar process can happen on Mars. The cations of martian sulfates would normally come from the weathering of martian igneous minerals. In this study, four cations (Fe^{3+} , Fe^{2+} , Mg^{2+} , Al^{3+}) important for Mars are used for synthesis. The goal of this comprehensive spectroscopic investigation (Raman, MIR, VIS-NIR, LIBS, and XRD) is to build the linkage between the laboratory spectroscopic characters with data from Mars, including the surface explorations and the orbital remote sensing.

Synthesis of copiapite minerals: Four copiapites [copiapite($\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$);magnescopiapite($\text{Mg}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$);ferricopiapite($\text{Fe}_2^{3+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$);aluminocopiapite($\text{Al}_2^{3+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$)] were synthesized in our laboratory. Materials used were $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ providing cations for various copiapite. The chemical reactions involved are as follows.

For bivalent cations (where $\text{X}=\text{Fe}^{2+}$, Mg^{2+}) copiapites:
 $\text{XSO}_4 + 2\text{Fe}_2(\text{SO}_4)_3 + 22\text{H}_2\text{O} \rightarrow$
 $\text{XFe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O} + \text{H}_2\text{SO}_4.$

For trivalent cations (where $\text{Y}=\text{Fe}^{3+}$, Al^{3+}) copiapites:
 $1/3\text{Y}_2(\text{SO}_4)_3 + 2\text{Fe}_2(\text{SO}_4)_3 + 22\text{H}_2\text{O} \rightarrow$
 $\text{Y}_{2/3}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O} + \text{H}_2\text{SO}_4$

The synthesis methods were based on the reports made by Friedlander and Majzlan [7, 8]. The saturated aqueous solutions were made by mixing different reagents with distilled water and H_2SO_4 . The copiapites were crystallized from the solution after days in an oven at 60°C . The remained H_2SO_4 in the powder samples were washed off using ethanol. Their structures were confirmed by XRD (a Rigaku Geigerflex X-ray diffractometer with a $\text{CuK}\alpha$ radiation source). Their chemical compositions were verified by laser-induced breakdown spectroscopy (LIBS, with a Continuum MiniLite pulse laser of 1064 nm, an Andor Mechelle 5000 spectrometer and DH734 ICCD).

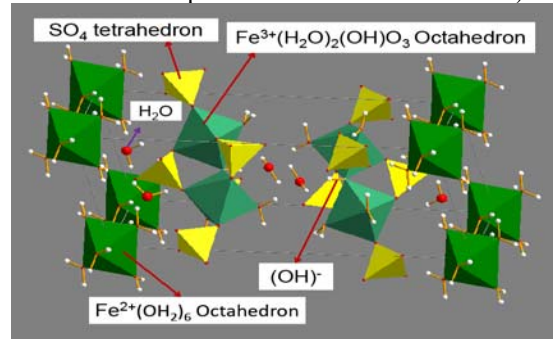


Figure 1: Copiapite crystal structure.

The crystal structure of copiapite: The copiapite structure (Fig. 1) is built by isolated octahedra (S octahedron = $[\text{X}(\text{OH})_6]$) and chains of tetrahedra (SO_4)-octahedra (C octahedron = $\text{Fe}^{3+}(\text{H}_2\text{O})_2(\text{OH})\text{O}_3$) [9]. Usually, the cation substitutions ($\text{X}=\text{Fe}^{3+}$, Fe^{2+} , Mg^{2+} , Al^{3+}) take place at S octahedral sites, while the four Fe^{3+} cations occupy the C octahedral sites. There are six free water molecules per copiapite formula unit. Two C octahedra are connected by sharing (OH). They also share coordinating oxygen with SO_4 tetrahedra thus making a stable chain sub-structure. Hydrogen bonding helps to connect S octahedra with the entire framework. There are three crystallographic distinct SO_4 sites per copiapite formula unit.

The four copiapites all belong to space group $\text{P}\bar{1}$ (C_i). The total vibration modes: $\Gamma^{\text{crystal}}_{\text{total}} = \Gamma^{\text{SO}_4} + \Gamma^{\text{OH}} + \Gamma^{\text{H}_2\text{O}} + \Gamma^{\text{Fc}} - \Gamma^{\text{acoust}} = (45\text{A}_g + 45\text{A}_u) + (6\text{A}_g + 6\text{A}_u) + (90\text{A}_g + 90\text{A}_u) + (6\text{A}_g + 9\text{A}_u) - 3\text{A}_u = 147\text{A}_g(\text{R}) + 147\text{A}_u(\text{IR})$. Therefore copiapite minerals have 294 fundamental vibration modes, 147 in Raman and 147 in Mid-IR spectra. However, not all these modes can

be detected; strong covalent bonds generally contribute most intense peaks in Raman and Mid-IR spectra. In copiapites spectra, the strongest peaks are contributed by the vibration modes of $(\text{SO}_4)^{2-}$, H_2O and $(\text{OH})^-$. The peaks in $900\text{--}1300\text{ cm}^{-1}$ region are from the symmetrical (v_1) and asymmetrical (v_3) stretching vibration modes of the SO_4 tetrahedra, and the peaks in $400\text{--}700\text{ cm}^{-1}$ region are from their symmetrical (v_2) and asymmetrical (v_4) bending vibration modes.

Raman, MIR, and VIS-NIR Spectroscopic Studies:

For all four copiapite samples, a HoloLab5000-532 laser Raman spectrometer (Kaiser Optical Systems Inc.) was used to obtain Raman spectra of $4000\text{--}100\text{ cm}^{-1}$; a Nexus 670 FTIR spectrometer for ATR Mid-IR spectra ($4000\text{--}400\text{ cm}^{-1}$); and an Analytical Spectral Device (ASD) for reflectance spectra of $400\text{--}2500\text{ nm}$.

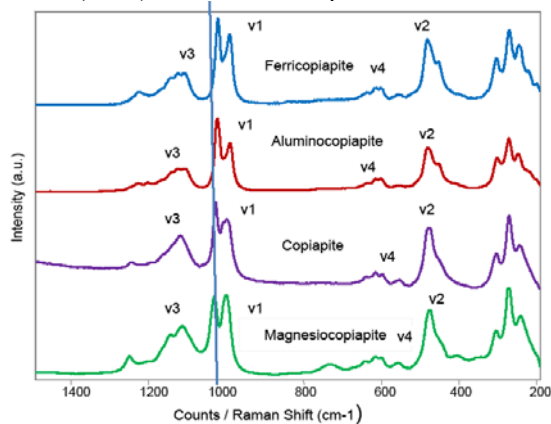


Figure 2: Raman spectra of four copiapites

Raman spectra of four copiapites are shown in Figure 2. A vertical line indicates the v_1 peak, which is the strongest in the Raman spectra of copiapites. In copiapite structure, there are three crystallographic distinct sites for the SO_4 tetrahedra. The environmental differences surrounding these SO_4 tetrahedra would induce the variation in the symmetry of three types of SO_4 tetrahedra and can lead to the splitting of v_1 vibration mode. In Figure 2, two obvious v_1 peaks of the SO_4 tetrahedra are seen in all spectra. An additional shoulder shows on v_1 peak of Fe^{2+} -copiapite. Different cations with different radius and mass in S octahedral sites can also influence on the environment of the SO_4 tetrahedra, which normally lead to the position shifts of its v_1 peak. Figure 2 shows the Raman peak shifts of Fe^{3+} , Fe^{2+} , Al^{3+} copiapites relative to Mg^{2+} -copiapite,

Mid-IR spectra of copiapites are shown in Figure 3. The v_3 mode of the SO_4 tetrahedra is the strongest in MIR spectra. This peak also shifts among the copiapites with different cations in S sites. Following the selection rules, the v_1 peaks of the SO_4 tetrahedra should be weak in the infrared spectra. It is, however, very strong for copiapites. The ultra low site symmetry

of the SO_4 tetrahedra due to the low symmetry of the copiapite structure should account for the breaking of selection rule.

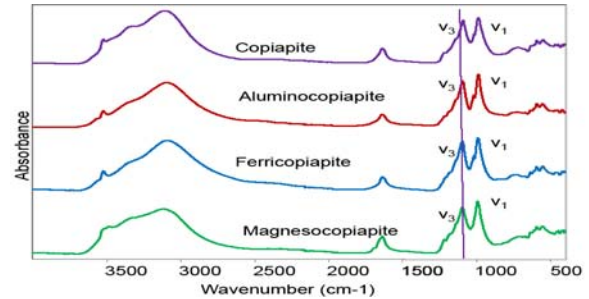
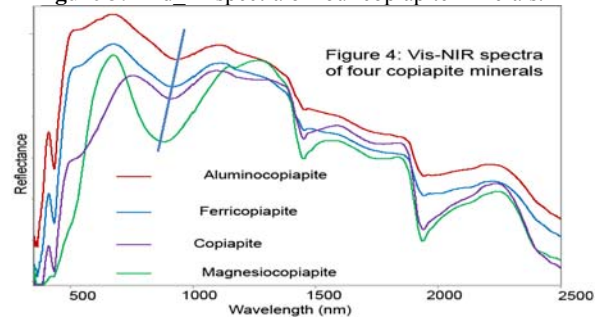


Figure 3: Mid-IR spectra of four copiapite minerals.



Vis-NIR spectra ($400\text{--}2500\text{ nm}$) of four copiapites are shown in Figure 4. Sharp absorption band caused by Fe^{3+} appear around 500 nm . In $800\text{--}1000\text{ nm}$ region, the absorption band shifts to lower wavelength indicated by a line. All copiapites show diagnostic absorption bands around 1450 and 1935 nm , as the combination modes of $(\text{SO}_4)^{2-}$, H_2O , and $(\text{OH})^-$. Detailed assignments will be presented at the conference.

Conclusions: Four copiapites were successfully synthesized and confirmed, structurally and compositionally, by both XRD and LIBS. Vibration modes are discussed based on space group theory. Raman, Vis-NIR, Mid-IR spectroscopic study were taken on these samples. The Raman spectra will be used for *in situ* mineral identification on Mars (Exomars), while the Vis-NIR and Mid-IR will be used to compare with the remote sensing data from Mars.

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References: [1] Klingelhöfer G. et al. (2004) *Science*, V306, 1740-1746. [2] Wang A. et al. (2006) *JGR*, V111, E02S17. [3] Wang A et al. (2007) *7th Mars 2007*, Abstract #3348. [4] Morris R. V. et al. (2006) *JGR*, V111, E02S13. [5] Johnson J. R. et al. (2007) *GRL*, V34, L13202. [6] Lane M. D. et al. (2008) *Am. Mineral.* 93, 728-739 [7] Friedlander et al. (2007) *LPSC*, XXXVIII, Abstract #2049. [8] Majzlan J. et al. (2006) *Euro. J. of Min.* V 18. 176-186. [9] Majzlan J. et al. (2006) *Can. Mineral.* 44, 1227-1237.