

PRELIMINARY EXPERIMENTS IN THE SYSTEMATIC INVESTIGATION OF THE SPECTROSCOPIC PROPERTIES OF SYNTHETIC COPIAPITE GROUP MINERALS. L. R. Friedlander¹, N.J. Tosca², R.E. Arvidson¹, ¹Washington University in St. Louis, ²SUNY, Stony Brook.

Introduction: Iron (jarosite in sedimentary rocks at Meridiani Planum), magnesium (kieserite, polyhydrated sulfates exposed in Valles Marineris and Terra Meridiani [1,2]) and calcium (gypsum exposed in north polar dunes [3] and in both Valles Marineris and Meridiani Planum [2-5]) sulfates have been identified by OMEGA and Opportunity on Mars. Iron (III) sulfate bearing minerals that display strong 6 micrometer water absorptions have been identified in light toned soils by Spirit [6-8]. The prevalence of hydroxylated and hydrated sulfate bearing minerals in Martian soils indicates a geochemical environment driven by acidic aqueous alteration and deposition. The copiapite family of mixed valence, hydrated sulfates is common to acidic terrestrial geochemical systems and is likely to be present on the Martian surface as well.

Copiapite displays frequent cationic substitutions and high sensitivity to relative humidity. Understanding how these properties change the spectral signatures of copiapite-group minerals aids in rigorous interpretation of remote sensing data both from terrestrial and Martian sites. We have pursued a detailed laboratory-based synthesis and analysis of the hydrated sulfate copiapite mineral group. Our goals were to synthesize various copiapite end members and investigate their *in-situ* and remote spectroscopic properties as functions of composition and relative humidity. The focus of this study is on successful synthesis of these minerals and the refinement of identification techniques.

We found that exposure to heat and maintenance of solution pH in the range of 0.0-1.5 were necessary for successful copiapite end member syntheses. Cation substitution was identified by X-ray diffraction and SEM measurements of end members with the substitution of 3+ cations in the 2+ cation lattice positions. This observation results from size-differences among 2+ and 3+ cations causing changes in unit cell dimensions, crystal habits and XRD patterns for such end-members (Figure 1). Simple 2+ substituted species are difficult to distinguish by XRD, although these species can be distinguished by cationic electronic absorptions in the UV wavelength region. Future work will examine the spectral characteristics of cationically differentiated copiapite-group end-members in the IR and UV-visible wavelength regions.

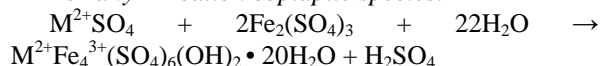
Methods: Six copiapite-group minerals were synthesized. Additionally, five mixed 2+ cation substituted salts of varying Fe²⁺/Zn²⁺ substitution ratios (10% Zn to 90% Zn by mole), were also synthesized.

Mineral name	Formula
Copiapite (proper)	Fe ²⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O
Magnesiocopiapite	Mg ²⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O
Zincocopiapite	Zn ²⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O
Manganocopiapite	Mn ²⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O
Ferricocopiapite	Fe _{2/3} ³⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O
Aluminocopiapite	Al _{2/3} ³⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O

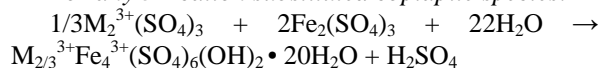
Table 1: Names and chemical formulas of successful syntheses.

Variably substituted copiapite minerals were prepared and isolated using two synthesis techniques. The first technique is based on a fixed mass of ~5.0g for the reagent Fe₂(SO₄)₃ • xH₂O and a fixed mass of H₂SO₄ (reagent grade 97% H₂SO₄, ρ=1.84g/mL) of ~1.1g. The amount of acid added was calculated to maintain a pH range within 0.0-1.5, with remaining reagents added according to the stoichiometric ratios given by the following reactions:

For any 2+ cation copiapite species:



For any 3+ cation substituted copiapite species:



Total solution mass was normalized to 15.0g by the addition of deionized water. Solutions were then placed in a 63.2°C oven for ~12 hours allowing partial evaporation and crystallization.

The second synthesis technique is a variation of the Majzlan synthesis [9]. Ferricocopiapite was produced by adding 40.8g of Fe₂(SO₄)₃ • xH₂O to 19.2g of deionized water to give a solution mass of 60.0g. Aluminocopiapite was produced by adding 34.05g of Fe₂(SO₄)₃ • xH₂O and 11.33g Al₂(SO₄)₃ • 18H₂O to 14.62g of deionized water. Both solutions were placed in a sonicator for >1 hour, allowed to stand at room temperature for 20 hours and placed in a ~60°C oven for 16 hours.

All samples were separated by centrifuge, filtered, washed in ethanol, dried at room temperature and divided among relative humidity buffers.

X-ray diffraction data were acquired using a Scintag PAD-X powder X-ray diffractometer over a 2theta range of 3-30 degrees. XRD samples were ground under ethanol, placed on glass slides, covered in thin plastic film, and immediately analyzed. SEM data and images were acquired using a LEO 1550 SFEG.

Results: Copiapite displays a platy crystal habit (Figure 2), resulting in preferred orientation scattering in XRD. The effects of preferred orientation are shown in our XRD results by disproportionate intensities of the peak at ~ 10 degrees 2θ . Substituted copiapite minerals display this peak at slightly different values of 2θ than those shown by copiapite proper or ferricopiapite. Identification of 3+ substituted species from 2+ substituted species is possible by XRD pattern. Characterization among 2+ substituted end members has not yet been accomplished. The ~ 10 degree peak is diagnostic [10] and provides positive identification for copiapite-group minerals (Figure 1). XRD results from ferricopiapite showing random scattering give evidence of low-angle copiapite reflections (Figure 1).

The effects of ambient conditions on copiapite mineral syntheses were observed in the production of sulfate side products. The stability of formation of such products is largely a function of pH. The most frequently observed contaminant was rhomboclase. Correcting solution pH to account for fluctuations during crystallization limited the production of rhomboclase. The presence of additional minerals related to the copiapite family is confirmed by SEM data, particularly in our Fe/S ratios which differ from idealized copiapite-group ratios and imply the formation of other synthetic sulfates within our copiapite samples.

Sample	Ratio	Species	Ideal Ratio
Fe2_S2	0.81	Copiapite	0.83
Fe3_S3	0.70	Fe-copiapite	0.78
Al_S4	0.80	Mg-copiapite	0.78
Mg_S12	0.70	Al-copiapite	0.83

Table 2: Comparison of synthetic Fe/S SEM ratios to idealized Fe/S SEM ratios of known samples.

Conclusion: Copiapite-group minerals were synthesized in the laboratory by careful application of known stability ranges and thermodynamic properties. Paragenesis hampered successful copiapite end-member characterizations. Our syntheses confirmed earlier observations of mineral paragenesis and dependence on ambient conditions [11,12]. Syntheses of dominantly pure end-member samples showed cation substitution producing distinct crystal habits (Figure 1). Sensitivity to relative humidity increased the difficulty of laboratory work with these samples, requiring the use of multiple techniques for characterization.

As part of a systematic study to individually characterize the spectral properties of the copiapite-group minerals, these initial experiments show that X-ray diffraction patterns can be individually assigned by

species and cation substitution. In the future, the IR and UV-visible wavelength region spectral signatures of copiapite-group end members will also be individually characterized.

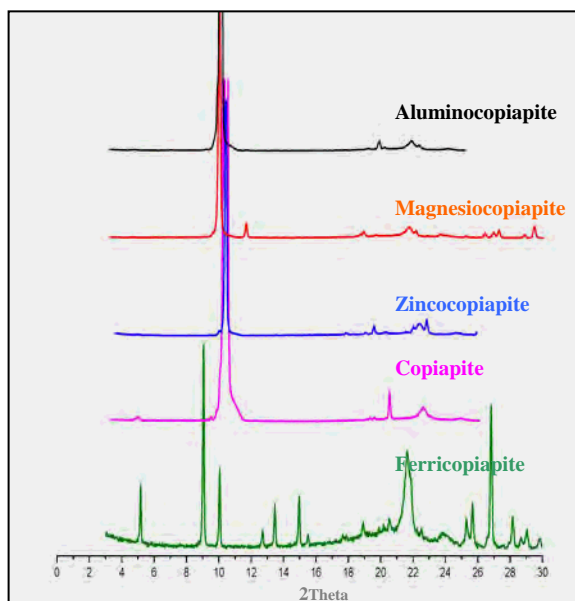


Figure 1: X-ray diffraction pattern for 5 synthetic minerals, relative intensity shown by count.

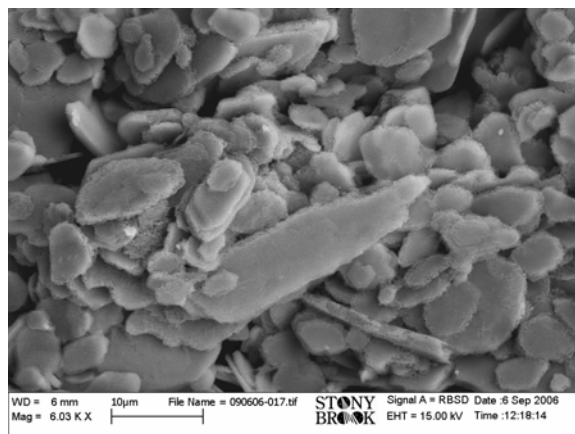


Figure 2: SEM produced image of the crystal habit of synthetic Copiapite.

References: [1] Squyres, S.W., et al. (2005) *E. and P. Sci. Letters*, 240. [2] Clark, B.C., et al. (2005) *E. and P. Sci. Letters*, 240. [3] Langevin, Y., et al. (2005) *Science*, 307. [4] McLennan, S.M., et al. (2005) *E. and P. Sci. Letters*, 240. [5] Gendrin, A., et al. (2005) *Science*, 307. [6] Gellert, R., et al. (2004) *Science*, 305. [7] Lane, M.D., et al. (2006) *LPS XXXVII*, Abstract #1799. [8] Bishop, J.L., et al. (2006) *LPS XXXVII*, Abstract #1438. [9] Majzlan, J., et al. (2006) *Euro. J. of Min.*, 18. [10] Atencio, D., et al. (1996) *Anais Assoc. Bras. Quím.*, 45. [11] Jamieson, H.E., et al. (2005) *Chem. Geo.*, 215. [12] Jerz, J.K., et al. (2003) *Am. Min.*, 88.