SPECTRAL PROPERTIES OF COPIAPITES WITH VARIABLE CATION COMPOSITIONS AND IMPLICATIONS FOR CHARACTERIZATION OF COPIAPITE ON MARS.

J. L. Bishop[1] , M. D. Dyar[2], J. Majzlan[3], and M. D. Lane[4], [1]SETI Institute/NASA-ARC (Mountain View, CA, 94043, jbishop@seti.org), [2]Mount Holyoke College (South Hadley, MA, 01075, mddyar@amherst.edu), [3]Institute of Mineralogy and Geochemistry (University of Freiburg, Freiburg, D-79104, Germany, juraj.majzlan@minpet.uni-freiburg.de), [4]Planetary Science Institute (Tucson, AZ, 85705-8331, lane@psi.edu).

Introduction: The hydrated iron sulfate copiapite may be an important component of the surface material on Mars. Copiapite was found to be consistent with the spectral and chemical data for the bright salty soils exposed at Paso Robles by the rover wheels [1]. Lab experiments also showed that copiapite dehydrated to 300 °C exhibits a unique visible/near-infrared (VNIR) band at 2.23 µm that is observed by CRISM in bright layered outcrops near Juventae Chasma [2, 3]. Copiapites exhibit a mid-IR doublet near 6.1 and 7.2 µm [4] that has been observed in the Martian dust by TES [5]. VNIR copiapite features are due to H_2O, OH and Fe [6, 7] and are consistent with the polyhydrated iron sulfate features observed by CRISM in layered deposits in the Valles Marineris region [3, 8, 9].

Samples: A large suite of copiapite samples was synthesized in order to examine the effects of variable Fe, Mg and Al cation abundances on the mineral structure and properties [10, 11]. The copiapite group minerals share the general formula:

$$[Fe^{3+}_2(OH)(H_2O)_4(SO_4)_3]_2[A(H_2O_6](H_2O)_6,$$

where A = Fe^{2+}, Fe^{3+}, Al, Mg, Cu, Ca, and/or Zn [12]. The structure includes layers of the [$A(H_2O_6)$] octahedra that are linked to the [$Fe^{3+}_2(OH)(H_2O)_4(SO_4)_3$] layers, forming [$M_2(SO_4)_2(O,H_2O)_7$] clusters.

Table 1 "*A*" site cation abundances

JB836	MAC-5:	$Mg_{0.41}Al_{0.29}Fe_{0.10}$
JB837	MAC-7:	$Mg_{0.97}Al_{0.02}$
JB839	FAC-1:	$Al_{0.59}Fe_{0.08}$
JB841	FAC-5:	$Al_{0.50}Fe_{0.16}$
JB843	FAC-10:	$Fe_{0.66}$

Results: Ten samples were selected from this previous study for characterization by Mössbauer, reflectance, and emission spectroscopy; typical spectra are shown here in Figures 1-3. "*A*" site occupancies for these samples are given in Table 1. Emission spectra are underway as well.

VNIR reflectance spectra (Figure 1). The primary Fe^{3+} electronic absorption for copiapite occurs at 0.86 µm and is accompanied by a weak band at 0.53 µm and a sharp band at 0.43 µm. Strong H_2O modes occur near 2.8-3.2 µm that result in an overtone at 1.45 µm, a combination band near 1.94 µm and a broad shoulder feature from 2.4-2.6 µm. Our spectra show additional water bands near 1.98 µm for the Fe-rich copiapites and near 2.01 µm for the Al-rich copiapites. OH stretching combination bands are observed in the 2.2-2.5 µm region and are present in the copiapite spectra as a weak dip from 2.20-2.25 µm, and as weak features near 2.46 and 2.52 µm in the Mg-rich samples and at 2.46 and 2.54 µm in the Al- and Fe-rich samples.

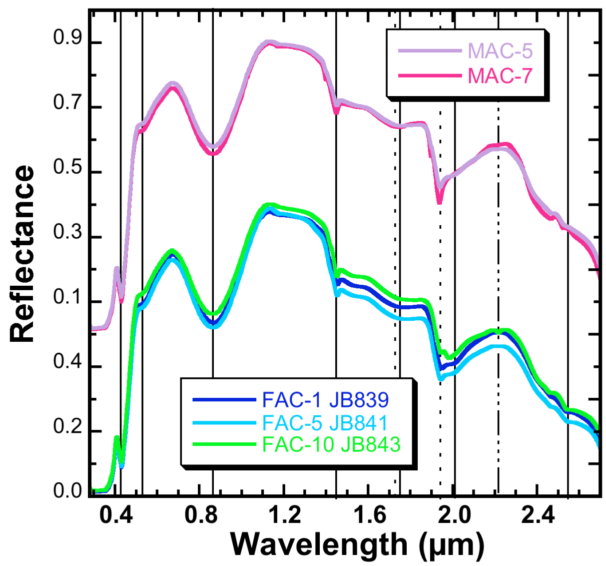

Figure 1 VNIR reflectance spectra of copiapites.

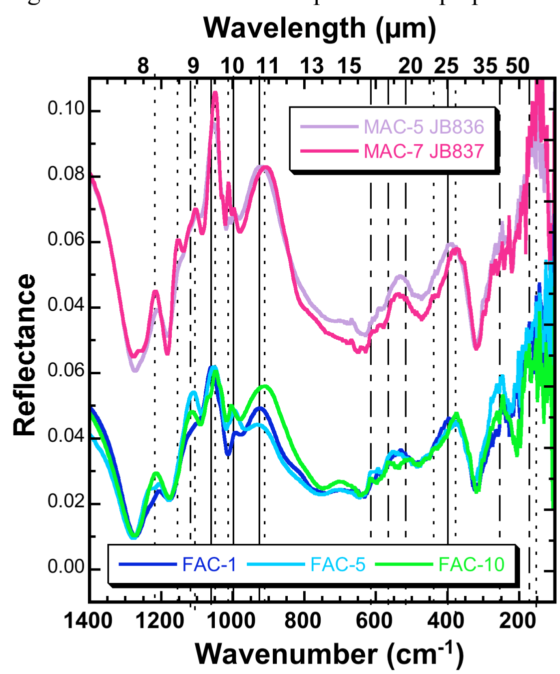

Figure 2 Mid-IR reflectance spectra of copiapites.

Mid-IR reflectance spectra (Figure 2). Copiapites have bands due to ν1, ν2, ν3 and ν4 sulfate vibrations in this region [13]. Our spectra show variations in the vibrational energies of the sulfate groups depending on the Fe-Al-Mg abundances. ν3 bands are observed near 1220, ~1116, and 1050 cm^{-1}, where the latter band is found at 1060 cm^{-1} for Al–rich and 1045 cm^{-1} for Mg- and Fe-rich samples. ν1 shifts from 993 cm^{-1} for the Al-rich to 1003 cm^{-1} for the Fe-rich to 1011 cm^{-1} for the Mg-rich samples. The ν4 bands occur at 610 and 563 cm^{-1} for the Fe-rich samples with an additional band at 515 cm^{-1} probably due to an OH-bending mode. The ν2 bands are observed at 443 and 377 cm^{-1} for the Mg- and Fe-rich samples, but only one band near 400 is observed for the Al-rich sample. Lattice modes are observed near 250 and 170 cm^{-1}, but are difficult to characterize due to spectral noise.

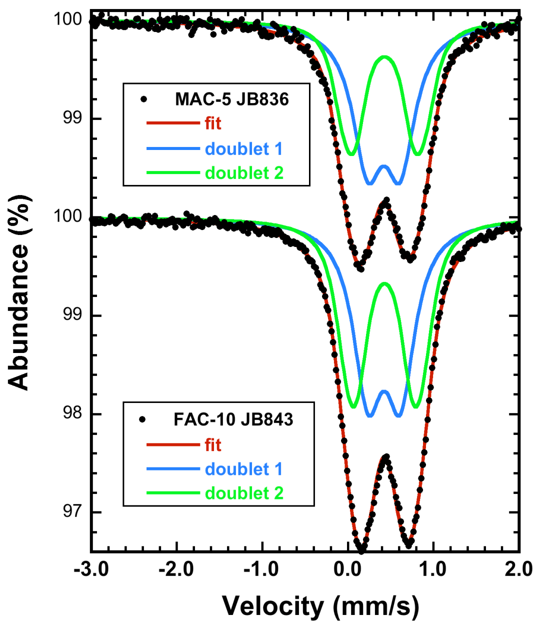

Figure 3 RT Mössbauer spectra of copiapites.

Mössbauer spectra (Figure 3, Table 2). The copiapite samples have only Fe^{3+}, fit with two distinct doublets sharing the same δ = 0.42-0.43 mm/s, but different quadrupole splittings: Δ = 0.36-0.40 mm/s for one and 0.77-0.80 mm/s for the other (Table 1). These two distributions do not correspond to the crystallographically-distinct sites in *i)* the [$A(H_2O_6)$] octahedra and *ii)* the sulfate layers because the parameter areas do not correspond to the ratios of $^{[A]}Fe^{3+}$:$^{[layer]}Fe^{3+}$, which would be 0.66:2 in sample FAC-10. Ongoing work is investigating this further. Two similar sites were observed in Mössbauer spectra of samples from the Río Tinto basin in Spain [14]: δ = 0.37 and 0.39 mm/s and Δ = 0.34 mm/s and 0.74 mm/s, respectively. The MAC (Mg-Al) series tends to have slightly higher Δ values in the smaller doublet (0.67-0.80 mm/s) compared to that of the FAC (Fe-Al) series (0.65-0.66 mm/s). The MAC samples have more Fe^{3+} in the first doublet compared to the second, while the FAC samples have a higher area for the second one.

Table 2 Mössbauer parameters for Fe^{3+} sites

	δ(mm/s)	Δ(mm/s)	Γ(mm/s)	Area(%)
MAC-5:	0.42	0.37	0.42	56
	0.43	0.67	0.26	44
MAC-7:	0.41	0.36	0.35	54
	0.42	0.80	0.30	46
FAC-1:	0.41	0.36	0.40	42
	0.42	0.65	0.30	58
FAC-5:	0.42	0.37	0.37	44
	0.43	0.66	0.30	56
FAC-10:	0.42	0.37	0.41	50
	0.43	0.65	0.30	50

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