

INTEGRATED SPECTROSCOPIC STUDIES OF HYDROUS SULFATE MINERALS. M.D. Dyar¹, M.D. Lane², J.L. Bishop², V. O'Connor⁴, E. Cloutis⁵, and T. Hiroi⁶. ¹Mount Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu; ²Planetary Science Institute, Tucson, AZ 85719; ³SETI Institute/NASA-Ames Research Ctr, Mountain View, CA, 94043; ⁴Dept. of Geology, Smith College, Northampton, MA 010XX, ⁵U. Winnipeg, Canada, ⁶Dept. of Geological Sci., Brown University, Providence, RI 02912.

Introduction: Sulfate minerals have been identified in Martian meteorites (e.g. [1]) and on Mars using a suite of instruments aboard the MER rovers [2]. These results have confirmed previous ground-based observations [3] and orbital measurements [4] that suggested their presence. The orbiting OMEGA instrument on Mars Express is also finding evidence for sulfate [5]. In order to better interpret remote-sensing data, we present here the results of a coordinated visible/near infrared (VNIR) reflectance, Mössbauer (MB), and thermal emittance study of well-characterized hydrous sulfate minerals.

Background: The majority of the hydrous sulfates are composed of (Mg,Fe,Mn) octahedra that share corners with H₂O and are connected by SO₄ tetrahedra. Our chemical analyses suggest that on Earth, solid substitution among species within mineral groups is common; much additional work will be needed to distinguish compositional differences across such solid substitutions. Furthermore, although virtually all of these phases are probably stable on Mars [6], many of them are barely stable under laboratory conditions (sometimes changing colors during handpicking!), so great care must be taken to measure their spectra under martian-like conditions. Table 1 shows a summary of phases that form the focus of our studies. Note that mineral species within individual groups usually have nearly identical structures and thus will have spectra that closely resemble one another, depending on the technique used for study.

Methods: Samples for this project (Table 1 and others not listed) were selected from the collections of coauthors; others came from the NMNH and the Harvard Mineralogical Museum. We have emphasized sampling from multiple localities so that compositional variability within groups could be assessed.

All mineral samples studied were first hand-picked to purify them, a step that was vitally important because many of these phases occur in intergrowths with other minerals. Some separates were then analyzed by XRD to confirm their purity and make unequivocal phase identifications and some remain to be done. Splits of the separates were made and distributed to RELAB for reflectance spectra and ASU for emittance spectra; Mössbauer measurements were made at Mount Holyoke College. Analytical methods used are described in [7].

Table 1. Samples Studied

Mineral Group	Mineral Species	Nominal Formula
kieserite	kieserite	Mg[SO ₄] · H ₂ O
	szomolnokite	Fe[SO ₄] · H ₂ O
	szmikite	Mn[SO ₄] · H ₂ O
starkeyite	starkeyite	Mg[SO ₄] · 4H ₂ O
	rozenite	Fe[SO ₄] · 4H ₂ O
	ilesite	Mn[SO ₄] · 4H ₂ O
pentahydrate	pentahydrate	Mg[SO ₄] · 5H ₂ O
	siderotil	Fe[SO ₄] · 5H ₂ O
hexahydrate	hexahydrate	Mg[SO ₄] · 6H ₂ O
melantherite	melantherite	Fe[SO ₄] · 7H ₂ O
epsomite	epsomite	Mg[SO ₄] · 7H ₂ O
rhombochase	rhombochase	Fe ³⁺ H[SO ₄] ₂ · 4H ₂ O
	lausenite	Fe ₂ ³⁺ [SO ₄] ₃ · 6H ₂ O
	kornelite	Fe ₂ ³⁺ [SO ₄] ₃ · (6+1/2)H ₂ O
	coquimbite	Fe ₂ ³⁺ [SO ₄] ₃ · (6+3)H ₂ O
	quenstedtite	Fe ₂ ³⁺ [SO ₄] ₃ · (9+2)H ₂ O
römerite	römerite	Fe ²⁺ Fe ₂ ³⁺ [SO ₄] ₄ · 14H ₂ O
halotrichite	pickeringite	MgAl ₂ [SO ₄] ₄ · 22H ₂ O
	halotrichite	Fe ²⁺ Al ₂ [SO ₄] ₄ · 22H ₂ O
	apjohnite	MnAl ₂ [SO ₄] ₄ · 22H ₂ O
	bilinite	Fe ²⁺ Fe ₂ ³⁺ [SO ₄] ₄ · 22H ₂ O
	krausite	KFe ³⁺ [SO ₄] ₂ · H ₂ O
voltaite	voltaite	K ₂ Fe ₅ ²⁺ Fe ₃ ³⁺ Al[SO ₄] ₁₂ · 18H ₂ O
	ferrinatriite	Na ₃ Fe ³⁺ [SO ₄] ₃ · 3H ₂ O
	goldichite	KFe ³⁺ [SO ₄] ₂ · 4H ₂ O
blödite	blödite	Na ₂ Mg[SO ₄] ₂ · 4H ₂ O
leonite	leonite	K ₂ Mg[SO ₄] ₂ · 4H ₂ O
polyhalite	polyhalite	K ₂ Ca ₂ Mg[SO ₄] ₄ · 2H ₂ O
gypsum	gypsum	Ca[SO ₄] · 2H ₂ O
	bassanite	Ca[SO ₄] · 1/2H ₂ O

Reflectance spectra: Visible/near-infrared reflectance spectra are shown in Fig. 1 from 0.3 to 5 μm to correspond to the spectra measured by OMEGA on Mars Express. These spectra exhibit features due to the SO₄²⁻ anion, Fe, OH and H₂O. Features due to Fe³⁺ occur from 0.4-0.9, while the broad bands near 1 μm are due to Fe²⁺. The strongest sulfate bands occur between 4 and 5 μm; other sulfate bands are observed near 1.75-1.85 and 2.2-2.5 μm. OH features occur near 1.4 and 2.2-2.3 μm, while bound water is responsible

for the broad band near 3 μm , plus weaker bands near 1.45 and 1.95 μm .

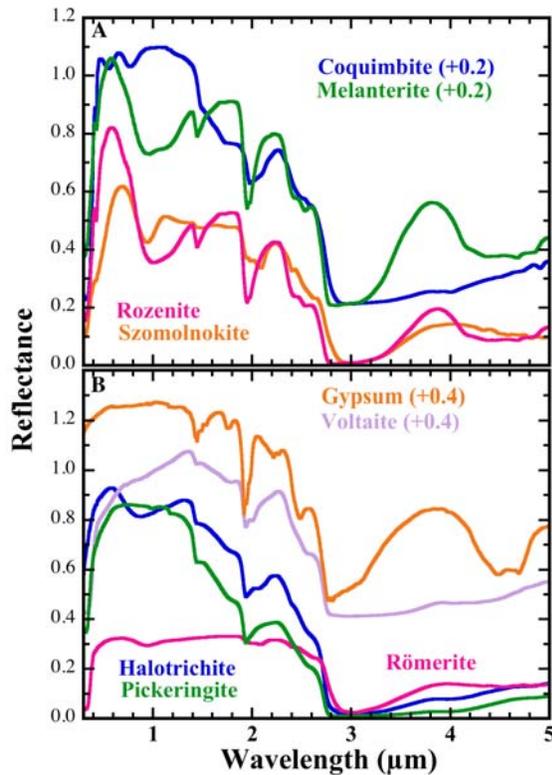


Fig. 1: VNIR spectra of selected sulfate minerals (all are powders: gypsum is $<63 \mu\text{m}$ particle size, szomolnokite and coquimbite are $<125 \mu\text{m}$, others are $<45 \mu\text{m}$).

Emissivity spectra: Only one spectrum from each mineral group is shown in Fig. 2 due to space constraints. All spectra exhibit features resulting from the fundamental vibrations of the SO_4^{2-} anion. Fundamental vibrational bands (some of which are split into 2 or 3 components) occur at $\sim 1050\text{-}1250$ (ν_3), ~ 1000 (ν_1), $\sim 500\text{-}700$ (ν_4), and $\sim 400\text{-}500$ (ν_2) cm^{-1} . Finer-grained samples such as melanterite and halotrichite show additional volume scattering features. The spectra of kieserite and hexahydrate are virtually identical due to their similar chemical composition and similar structure; however, XRD confirmed the mineral assignments. This emphasizes the need to understand both structures and chemistries of interrelated sulfates.

Mössbauer results: MB spectra of two voltaites at opposite ends of the Mg-Fe solid solution are shown in Fig. 3. Peak energies do not vary, but the relative line intensities change with composition. Similar trends are found in other hydrous sulfates, where Mg and Fe usually occupy the same site.

Conclusion: Our integrated studies of hydrous sulfates are just beginning. We anticipate that our even-

tual data set will allow cross-correlation of VNIR, IR, emissivity, and MB spectra and prove useful in interpretations of Mars mission data.

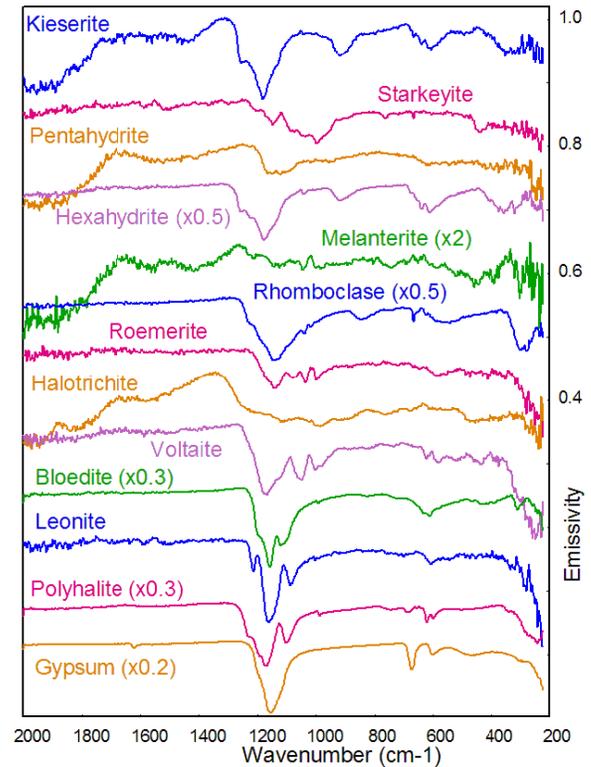


Fig. 2. Emissivity spectra of select hydrous sulfates.

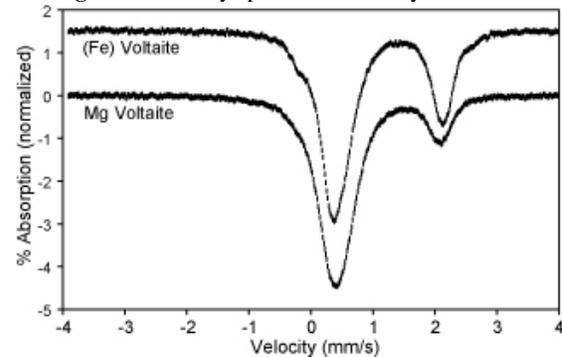


Fig 3. Mössbauer spectra of voltaites.

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