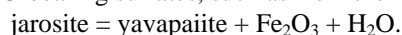


INTEGRATED SPECTROSCOPIC STUDIES OF ANHYDROUS SULFATE MINERALS. M. D. Lane¹, J. L. Bishop², M. D. Dyar³, E. Cloutis⁴, F. L. Forray⁵ and T. Hiroi⁶. ¹Planetary Science Institute, Tucson, AZ 85719. ²SETI Institute/NASA-Ames Research Center, Mountain View, CA 94043, ³Mount Holyoke College, South Hadley, MA 01075, ⁴Univ. of Winnipeg, Canada, ⁵Thermochemistry Facility and NEAT ORU, Univ. of Calif. Davis, Davis, CA 95616, ⁶Dept. of Geological Sci., Brown University, Providence, RI 02912.

Introduction: Sulfates have been identified in Martian soils and bedrock and are emerging as an important indicator for aqueous activity on Mars. Sulfate minerals can form in a variety of low-temperature (evaporitic; chemical-weathering) and high-temperature (volcanic/fumarolic; hydrothermal) environments and their formational environments can range from alkaline to acidic. Although sulfates generally form in the presence of water, *not all sulfates are hydrous or contain water in their structures.*

Many of these anhydrous sulfates (Dana group 28; Strunz class 67A) are minerals that form as accompanying phases to the main minerals in ore deposits or as replacement deposits in sedimentary rocks. However, some form from thermal decomposition of OH or H₂O-bearing sulfates, such as from the reaction [1]:



Where known, the stability fields of these minerals all suggest that they would be stable under martian surface conditions [2].

Thus, anhydrous sulfate minerals may contribute to martian surface mineralogy, so they must be well-represented in spectral libraries used for interpretation of the Martian surface. We present here the preliminary results of an integrated study of emittance, reflectance, and Mössbauer spectroscopy of a suite of well-characterized anhydrous sulfates.

Background: Anhydrous sulfates have structures composed of SO₄ groups linked with octahedra in various combinations. depending on the size of the cation (Table 1), the octahedra may be insular (yavapaiite), edge-sharing (thenardite), or face-sharing (aphthitalite). If the cations are larger, the polyhedra are higher in coordination; e.g., arcanite contains chains of edge- and face-sharing ⁹⁹K and ¹⁰¹K and anhydrite group minerals contain ⁸⁸Ca. On Earth, the most common of these structures is that of the barite group (barite, celestine, anglesite), in which the cation is 10-coordinated. Spectroscopically, we would expect these structures to share the fundamental transitions of the SO₄ groups, and vary according to the coordination polyhedra associated with their cations.

Methods: Samples for this project (Table 1) were generously made available to us by the NMNH (Smithsonian) and the Harvard Mineralogical Museum; some additional samples were from the authors' collections, and the yavapaiite was synthesized by co-

author Forray. All mineral samples studied were first hand-picked to purify them, a step which was vitally important because many of these phases occur in intergrowths with other minerals. The separates were then analyzed by XRD to confirm their purity and make unequivocal phase identifications. 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. All samples were kept in dry air in a desiccator when not being analyzed.

Visible to near-infrared (VNIR) bidirectional reflectance spectra (0.3 to 2.6 μm; 5 nm sampling resolution) were acquired relative to halon at 30° incident, 0° emergent angles. The same samples were measured under dehydrated conditions using a Pike diffuse reflectance attachment (off-axis, biconical) with the Nicolet 870 Nexus FTIR spectrometer (1 to 50 μm) using a diffuse gold standard. The FTIR data were typically spliced to the bidirectional data near 1.2 μm, in order to provide absolute reflectance.

Table 1. Samples Studied

Mineral Species	Nominal Formula
misenite ^{a,b}	K ₈ H ₆ (SO ₄) ₇
arcanite ^{a,b}	K ₂ SO ₄
aphthitalite ^{a,b}	(K,Na) ₃ Na(SO ₄) ₂
thenardite ^{a,b}	Na ₂ SO ₄
barite ^{a,b}	BaSO ₄
celestine ^{a,b}	SrSO ₄
anglesite ^{a,b}	PbSO ₄
anhydrite ^{a,b}	CaSO ₄
yavapaiite ^{a,b,c}	KFe ³⁺ (SO ₄) ₂
glauberite ^{a,b}	Na ₂ Ca(SO ₄) ₂

^a VNIR reflectance; ^b MIR emittance; ^c Mössbauer

The midinfrared (MIR) thermal emittance data (2000 to 200 cm⁻¹ at 2 cm⁻¹ sampling; 5 to 50 μm) were collected using modified Nicolet FT-IR spectrometer with a continuously scrubbed atmosphere and a room-temperature DTGS detector. The spectra of heated samples (~50-90 °C) were acquired over 160 scans.

Room temperature Mössbauer (MB) spectra were acquired to determine relative amounts of Fe²⁺ and Fe³⁺ when they were present in sufficient abundances to measure. Samples were prepared by mixing sample

powders with sugar (under acetone) and mounting in a sample holder confined by tape. A source of ~ 45 mCi ^{57}Co in Rh was used on a WEB Research Co. model W100 spectrometer. Run times ranged from 12-48 hours. Results were calibrated against α -Fe foil of 6 μm thickness and 99% purity.

Results: Reflectance spectra: VNIR data are shown for the range measured by OMEGA (Fig. 1). These spectra exhibit sulfate overtone and combination bands near 1.75-1.85, 2.2-2.5 and 4-5 μm . Some samples exhibit CH bands near 3.5 due to organic admixtures. Some spectra also contain OH/H₂O bands near 2.7-3.2 μm , although these shouldn't be present in the structure and the samples were carefully dehydrated before measurement. Sulfate is highly polarizable and even "anhydrous" sulfates may contain small amounts of OH/H₂O in some cases.

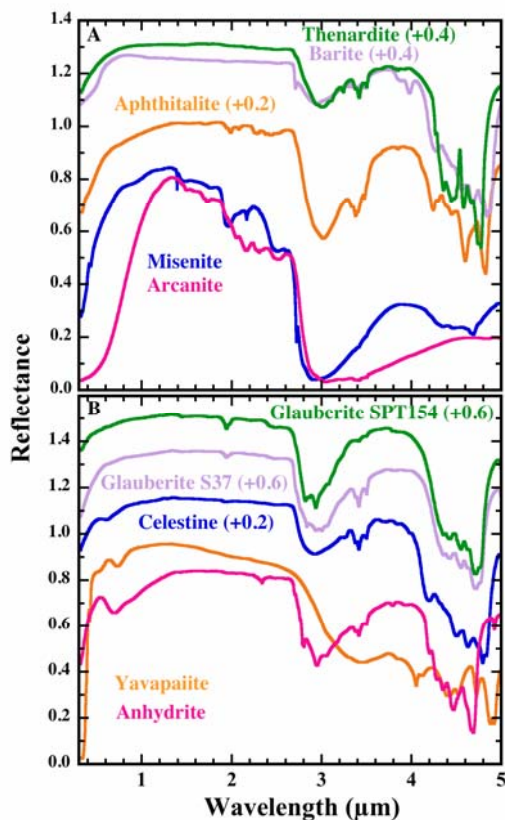


Fig. 1. VNIR spectra of anhydrous sulfates.

Emission spectra: All MIR spectra exhibit features resulting from the fundamental vibrations of the SO_4^{2-} anion (Fig. 2). Fundamental vibrational bands (some of which are split into 2 to 3 components) occur at ~ 1050 -1250 (ν_3), ~ 1000 (ν_1), ~ 500 -700 (ν_4), and ~ 400 -500 (ν_2) cm^{-1} . Finer-grained samples such as anhydrite and yavapaiite show additional volume scattering features. The spectra of misenite and arcanite

are virtually identical due to their similar chemical composition and similar structure.

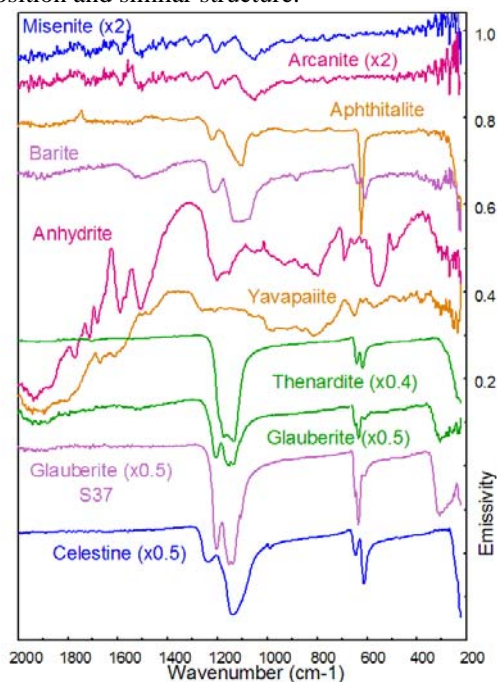


Fig. 2. Emission spectra of anhydrous sulfates.

Mössbauer: The 295K Mössbauer spectrum of yavapaiite is shown in Fig. 3. It has a single doublet characteristic of $^{56}\text{Fe}^{3+}$ with an isomer shift of 0.48 mm/s and a quadrupole splitting of 0.305 mm/s, as would be expected from insular Fe octahedra.

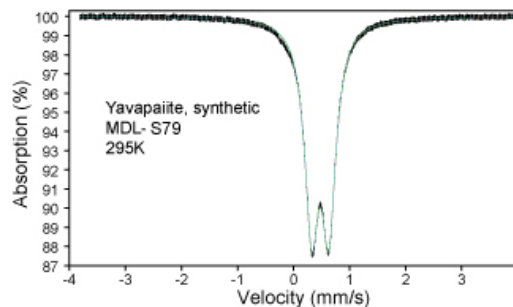


Fig. 3. First reported MB spectrum of yavapaiite.

Conclusion: Our integrated study is just beginning and we anticipate voluminous data that can be cross-correlated between VNIR, IR, and MB analyses and applied to the interpretation of Mars mission data.

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References: [1] Forray, F. L. et al. (2004) Second Conf. Early Mars, *abs. 8009*. [2] Forray, F. L. et al. (submitted).