IRON SULFATE AND SULFIDE SPECTROSCOPY AT THERMAL INFRARED WAVELENGTHS.

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Introduction: Ferric *sulfate* minerals were identified in several light-toned subsurface soils in Gusev Crater, Mars, that were exposed by the Mars Exploration Rover (*Spirit*) wheels. Although the identified ferric sulfate minerals vary from site to site [1-3], several different sulfates have been identified, including ferricopiapite (dominating the Paso Robles bright track soils) [2], (para)coquimbite, fibroferrite, rhomboclase, and hydronium jarosite, and possibly minor (para)butlerite or metahohmanite. Recent work by the Mars Reconnaissance Orbiter (MRO) CRISM (visible-near infrared) team suggests that the polyhydrated sulfates such as ferricopiapite may be widely present on Mars, and that ferricopiapite may be found in a partially dehydrated state in inverted channels in Juventae Chasma and other nearby Chasma in the Valles Marineris region [4]. A growing laboratory suite of ferric sulfate minerals (including the minerals mentioned above as well as many other ferric sulfates, some of which were dehydrated intentionally) have been analyzed using a thermal emission (mid-infrared) spectroscopic technique to continue to provide well-defined and well-understood emissivity spectra of a large range of ferric sulfate minerals in order to aid and expedite the identification of these minerals and their dehydration products using TES and Mini-TES (mid-infrared) emission data from Mars.

This work also includes thermal emission studies of a variety of *sulfide* minerals for a similar purpose of identifying them on Mars. Sulfides occur in terrestrial volcanic terrains similar to igneous terrains on Mars. On Earth sulfides are abundant in hydrothermal areas on land and undersea "black smokers" as seen and sampled by the submersible, *Alvin*, at the East Pacific Rise. Sulfides also are found in Martian meteorites. Hence, sulfides are an important mineral class to understand because they also are possible precursor minerals [5] that can follow an oxidation pathway (with proper hydration and pH) to form ferric sulfate and other sulfate minerals [e.g., 2,3,6].

Objective: We will present thermal emissivity spectra of: 1. a suite of ferric sulfates, 2. dehydrated ferric sulfates (dehydration products), and 3. a suite of sulfide minerals. All of these minerals have an application to interpretating mid-infrared data from Mars.

Ferric Sulfates: Ferric sulfates are formed by a series of oxidation, dehydration, and neutralization reactions [2] and are formed in low pH environments such as acid-mine drainage sites on Earth. Ferric sulfates form in generally similar conditions; however, their crystallography and emissivity spectra are quite diverse as evidenced by their varied spectra (Figure 1).

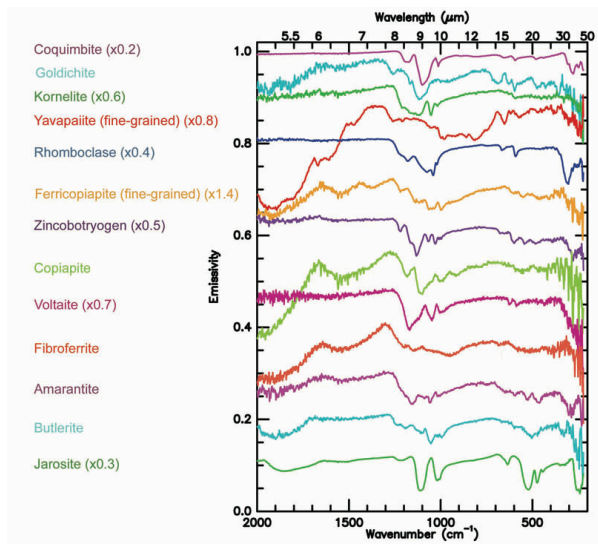

Figure 1. Thermal emissivity spectra of a suite of ferric sulfates. The spectra were acquired at the Mars Space Flight Facility at Arizona State University.

Dehydration of Ferric Sulfates: Two ferric sulfate samples were selected for dehydration measurements [4]. These samples included a synthetic kornelite (ML_S105) and a copiapite sample (JB787). The kornelite sample was measured when first synthesized, and later measured after natural (ambient) dehydration that caused the formation of rhomboclase and the sample color to change from light purple to yellow. The copiapite sample was measured in emissivity, then heated in a step-wise fashion to 100 ˚C, 200 ˚C, 250 ˚C, and finally 300 ˚C, holding the temperature for 30 minutes at each temperature increment. The final product was again measured to obtain the emissivity spectrum. These original sample spectra, as well as the dehydration product spectra are shown in Figure 2.

The dehydration experiments have direct application to understanding the surface of Mars and the potential for various sulfates to be formed and altered.

Recent studies of the CRISM team have found spectral evidence that significant amounts of ferricopiapite in a partially dehydrated state may occur on the surface of Mars in inverted channels in Juventae Chasma and other neaby Chasma in the Valles Marineris region.

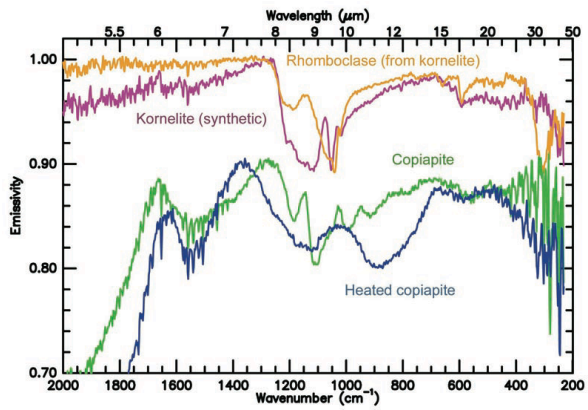

Figure 2. Thermal emissivity spectra of two samples that underwent change. The synthetic **kornelite** sample dehydrated under ambient conditions and altered to rhomboclase. The **copiapite** sample underwent stepwise heating to 300 °C.

Sulfides: Sulfide minerals are common in promitive Interplanetary Dust Particles [e.g., 7] and meteorites (and were detected in Comet Halley) [e.g., 8]. Sulfides likely occur throughout the solar system (e.g., Io, Europa, Ganymede [9], etc.), including being common in terrestrial volcanic terrains as well as in "black smokers" seen by the sub, *Alvin*, at the East Pacific Rise.

The thermal emissivity spectra of 11 sulfides are shown in Figure 3. Sulfides generally are spectrally flat (graybody) at the higher frequencies (higher wavenumbers) but exhibit spectral structure longward of ~450 cm^{-1}. The sulfide features dominate each spectrum from 450 to 200 cm^{-1} region [10].

Five samples collected from the East Pacific Rise black smokers have been analyzed in thermal emission. The spectra (not shown) show evidence for a variety of sulfate minerals (including gypsum and anhydrite) as well as spectral evidence for sulfides. Specifically, chalcopyrite and pyrite were identified on the basis of their thermal emissivity spectra alone.

Because Mars had extensive volcanic activity, sulfides ought to be present. Additionally, the bright ferric-sulfate bearing soils of Paso Robles (Mars) may have originated from the oxidation of precursor volcanogenic sulfide deposits [e.g., 2,3] as seen in terrestrial environments [e.g., 5]. Other sulfates on Mars, as well, may be derived from precursor sulfide minerals [e.g., 6].

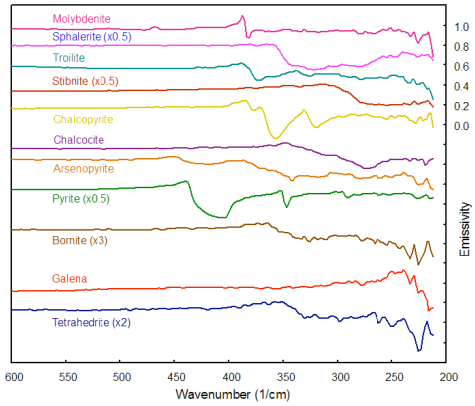

Figure 3: Thermal emissivity spectra of sulfide minerals over the 600 to 200 cm^{-1} region. Spectra are offset for clarity.

Conclusion: Sulfates and sulfides represent important minerals on the surface and in the interior of Mars (and are found in Martian meteorites). In order to identify these minerals in data sets returned from Mars, extensive laboratory analyses of well-characterized minerals must be conducted to produce high-quality thermal emission sample spectra for comparison. We will continue to study sulfate- and sulfide-suite minerals and apply our spectra to Martian data sets in order to better understand the environmental conditions on Mars, including oxidation, hydration, pH, etc. The sulfate and sulfide minerals studied here in the mid-infrared will be studied in a collaborative manner using visible-near infrared and Mössbauer techniques.

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