REFLECTANCE SPECTRA OF MONOHYDRATED SULFATES WITH VARIABLE Mg AND Fe ABUNDANCE, AND IMPLICATIONS FOR THEIR IDENTIFICATION ON MARS. Dominik Talla¹, Janice L. Bishop², Manfred Wildner¹, ¹University of Vienna (Vienna, Austria; dominik.talla@univie.ac.at), ²SETI Institute (Mountain View, CA).

Summary: Monohydrated sulfates (MHS) containing Mg and Fe provide important insights into the geochemistry of the martian fluids they crystallized from. This study of the spectral properties of synthetic Mg-Fe MHS reveals that even 5% Fe in kieserite (MgSO₄·H₂O) greatly alters its spectral properties, shifting the characteristic kieserite band at 2.13 µm towards shorter wavelengths. This study expands on a previous investigation of the IR and Raman spectra of synthetic Mg/Fe-MHS [1]. Shifts in the MHS lattice parameters with decreasing temperature are associated with changes in the spectral properties that could influence detection of these minerals on Mars [1].

Introduction: Hydrated sulfates are present across Mars with increased abundance near Valles Marineris, where a variety of MHS and polyhydrated sulfates (PHS) are observed [2]. Investigations of CRISM spectra have shown variation in the MHS spectral properties from kieserite to szomolnokite, (FeSO₄·H₂O), at locations including Juventae Chasma [3] and Meridiani Planum [4]. Thus, VNIR reflectance spectra of Mg/Fe-MHS may lead to better characterization of sulfate outcrops on Mars.

Methods: MHS samples with variable Mg and Fe abundance at 5% intervals were synthesized hydrothermally at 210 °C with a redox buffer to prevent oxidation of the Fe²⁺ in analogy to a previous study of their IR and Raman spectral properties [1]. XRD analyses documented changes in the lattice parameters as a function of Mg/Fe abundance (Fig. 1) and temperature from -160 to 40 °C [1].

Bulk reflectance spectra were measured using an ASD spectrometer at the SETI Institute. Then the samples were crushed and dry sieved to <250 and >250 µm size fractions, and reflectance spectra were collected using a bidirectional spectrometer (0.3-2.5 µm) and an off-axis biconical Nicolet FTIR spectrometer at

Fig. 1 View of crystal structures of kieserite (grey MgO₆ octahedra) over szomolnokite (green FeO₆) to illustrate changes in the shape of the octahedra with these cations. The SO₄ tetrahedra are depicted in yellow (from [1]).

Fig. 2 VNIR reflectance spectra of monohydrated sulfates with variable Mg-Fe abundance (<250 µm particle size) with lines marking band centers of the Fe-rich spectra. The 50% Mg/50% Fe MHS spectrum is shown in dark green with a dashed curve and Fe increases by 5% for each spectrum.

RELAB, Brown University.

Results: Visible/near-infrared (VNIR) reflectance spectra of this collection of Mg- and Fe-bearing MHS samples demonstrate that a strong Fe²⁺ crystal field theory band is present at 0.94 µm for samples containing as little as 5% Fe (Fig. 2). Additional changes are observed for the bands near 1.52-1.53 and 1.98-2.13 µm, but these shifts are gradual as the Fe increases to ~30%. The kieserite triplet at 1.978, 2.06, and 2.13 µm
narrow with increasing Fe concentration, producing a broadened band at \( \sim 2.09-2.10 \) \( \mu \text{m} \) and a shoulder near \( 1.99-2.00 \) \( \mu \text{m} \). The bands near 2.40 and 2.62 \( \mu \text{m} \) remain largely unchanged, irrespective of cation ratio.

Strong reflectance peaks occur near 1195 and 1260 \( \text{cm}^{-1} \) in spectra of kieserite and change to a triplet near 1160, 1200, and 1230 \( \text{cm}^{-1} \) in spectra of szomolnokite (Fig. 3). Generally, comparable features for szomolnokite (and also dwornikite, \( \text{NiSO}_4 \cdot \text{H}_2 \text{O} \)) are observed at lower wavenumbers in these reflectance spectra. This is similar to previous observations using the diffuse reflectance setup and undiluted sample material, where these features remain fairly constant, irrespective of the cation ratio [1,5].

**Fig. 3** Reflectance spectra of particulate monohydrated sulfate samples containing 0%, 20%, 50%, and 100% Fe to illustrate the major changes in spectra for these samples as Fe replaces Mg in the structure. Light blue lines mark bands in kieserite spectra, while rotten orange lines mark bands in szomolnokite spectra.

**Fig. 4** Reflectance spectra of different size fractions of kieserite. The band positions (marked by light blue lines) remain the same except for the transparency feature near 800 \( \text{cm}^{-1} \), observed only for the finer fraction. The near-IR combination bands are stronger in the spectra of the <125 \( \mu \text{m} \) size fraction as well.

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