

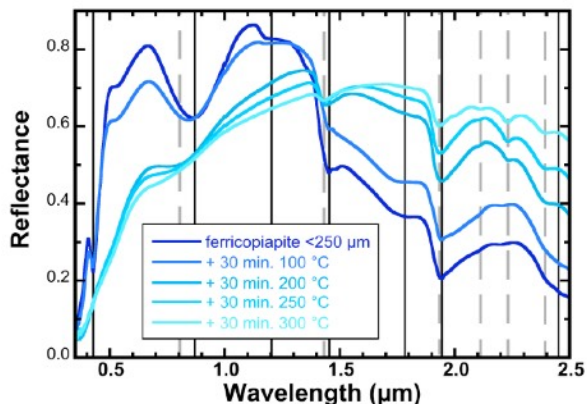
## SPECTRAL PROPERTIES OF FE HYDROXY SULFATES AND IMPLICATIONS FOR MARS.

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**Summary:** Reflectance and transmittance spectra of heated Fe-rich hydrated sulfates develop new spectral features as Fe-rich hydroxy sulfates are produced. These hydroxy sulfates exhibit unique spectral signatures that appear to explain unusual bands near 2.23  $\mu\text{m}$  found in orbital data of small outcrops in sulfate-rich regions. The  $\text{Fe}^{2+}\text{SO}_4\text{OH}$  spectrum contains bands at  $\sim 2.236$  and  $2.37$   $\mu\text{m}$ , while the  $\text{Mg}_{0.5}\text{Fe}^{2+}_{0.5}\text{SO}_4\text{OH}$  spectrum contains bands at  $2.226$  and  $2.4$   $\mu\text{m}$  that can be used for identifying these species on Mars with CRISM spectra. Several additional spectral bands are observed for these hydroxy sulfates and many of them parallel features observed in jarosite  $[\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6]$  spectra.

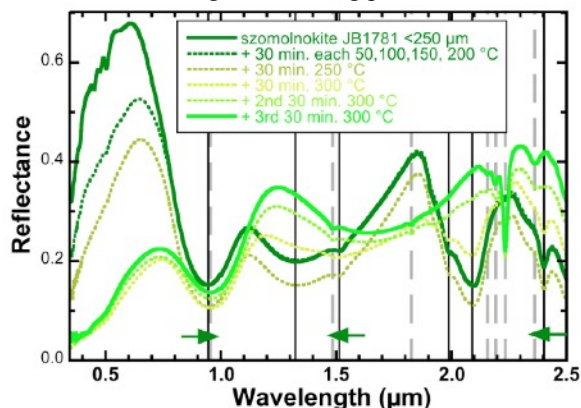
**Introduction:** Iron hydroxy sulfates have been attributed to unusual spectral features near  $2.23$  and  $2.4$   $\mu\text{m}$  observed in CRISM spectra of small outcrops in sulfate-rich regions at Juventae Chasma [1], Carpri Chasma [2] and Aram Chaos [3]. Previous lab experiments heating ferricopiapite  $[\text{Fe}^{3+}_{0.67}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}]$  to  $300$   $^\circ\text{C}$  [1] and melanterite  $[\text{Fe}^{2+}(\text{SO}_4) \cdot 7\text{H}_2\text{O}]$  to  $240$   $^\circ\text{C}$  [4] produced hydroxy sulfates with bands near  $2.23$   $\mu\text{m}$ . The spectrum of the dehydrated ferricopiapite sample contained weak bands near  $2.12$  and  $2.23$   $\mu\text{m}$  (Fig. 1) that disappeared over days despite desiccation, likely due to rehydration. This was a natural sample and may have contained some  $\text{Fe}^{2+}$  along with  $\text{Fe}^{3+}$  in the A site. The heated melanterite converted first to szomolnokite and then hydroxy sulfate in air, but formed anhydrous  $\text{Fe}^{2+}\text{SO}_4$  under  $\text{N}_2$  [4].

**Methods:** We used synthetic monohydrated sulfates (MHS) from [5,6] and rozenite  $[\text{Fe}^{2+}(\text{SO}_4) \cdot 4\text{H}_2\text{O}]$  from Iron Mountain [7] to test formation of hydroxy sulfate. The fine-grained rozenite had partially altered to szomolnokite since it was first studied. Each particulate sample was placed in a black teflon dish and exposed to

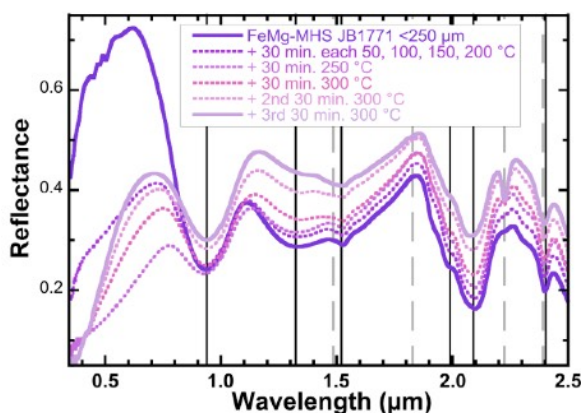


**Fig. 1** VNIR reflectance spectra of ferricopiapite (JB787-B) while progressively heating up to  $300$   $^\circ\text{C}$ .

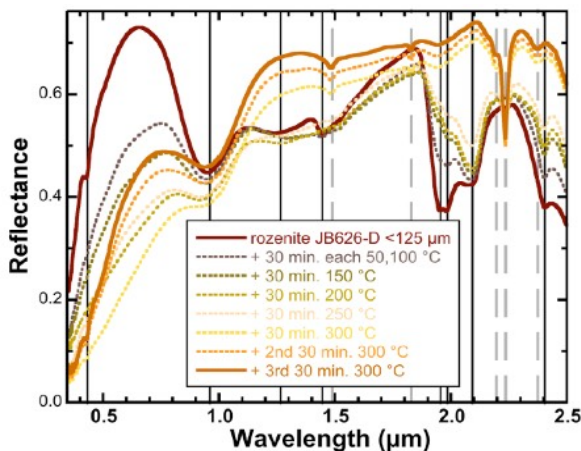
repeated heating for 30 min. intervals at progressively elevated temperatures up to  $300$   $^\circ\text{C}$ . VNIR spectra were measured with an ASD spectrometer under ambient conditions following each heating period.



**Fig. 2** VNIR reflectance spectra of szomolnokite (JB1781) while progressively heating up to  $300$   $^\circ\text{C}$ .

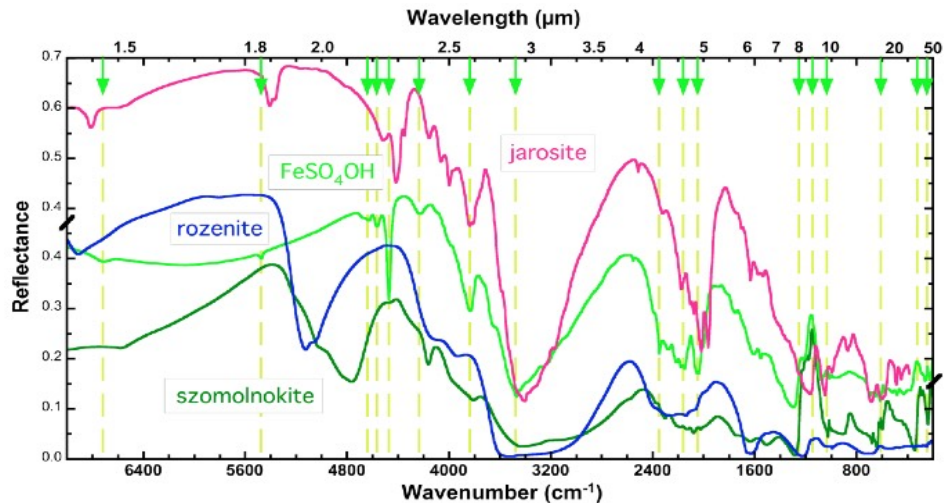


**Fig. 3** VNIR reflectance spectra of  $\text{Fe}_{0.5}\text{Mg}_{0.5}$ -MHS (JB1771) while progressively heating up to  $300$   $^\circ\text{C}$ .



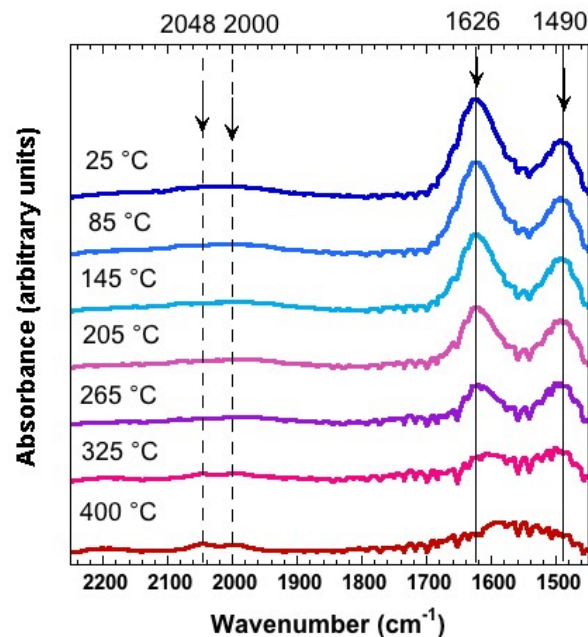
**Fig. 4** VNIR reflectance spectra of rozenite (JB626-D) while progressively heating up to  $300$   $^\circ\text{C}$ .

**Fig. 5** Reflectance spectra of Fe hydroxy sulfate, jarosite, szomolnokite, and rozenite. The jarosite and Fe hydroxy sulfate spectra are offset by 0.1. Spectral features due to Fe hydroxy sulfate are marked by light green dashed lines and green arrows. New NIR features are observed at 1.49, 1.83, 2.16, 2.19, 2.236, 2.37, 2.61, and 2.88  $\mu\text{m}$ . The strongest mid-IR bands occur at 2050 and 1155  $\text{cm}^{-1}$  ( $\sim 4.9$  and  $8.7$   $\mu\text{m}$ ).



Reflectance spectra were then measured of the hydroxy sulfate products at RELAB under dry conditions (Fig. 5). Transmittance spectra were measured continuously of rozenite/szomolnokite JB626-D with increasing temperature up to 400 °C under vacuum ( $\sim 0.7$  Torr) [8].

**Results:** VNIR reflectance spectra are shown with increasing temperature in Figs. 1-4 to illustrate evolution of the bands near 2.3  $\mu\text{m}$ . In contrast to the earlier study with ferricopiapite (Fig.1), little change was observed with heating in the position of the Fe crystal field bands at 0.94-0.95  $\mu\text{m}$  in szomolnokite (Fig. 2)



**Fig. 6** Changes in the transmittance spectra of hydrated Fe sulfate JB626-D with increasing temperature. The band at 1626  $\text{cm}^{-1}$  is due to  $\text{H}_2\text{O}$  in rozenite and the band at 1490  $\text{cm}^{-1}$  is due to  $\text{H}_2\text{O}$  in szomolnokite. As the temperature increases, these bands decrease in intensity and a doublet develops at 2000 and 2048  $\text{cm}^{-1}$ . Solid lines mark rozenite and szomolnokite bands, while dashed lines mark Fe hydroxy sulfate bands.

FeMg-MHS (Fig. 3), and rozenite (Fig. 4). The strong NIR bands resulting from heating MHS and rozenite occurred at 2.235-2.236 and  $\sim 2.37$   $\mu\text{m}$  for 100%  $\text{Fe}^{2+}$  and at 2.227 and  $\sim 2.4$   $\mu\text{m}$  for 50% $\text{Fe}^{2+}$ /50%Mg, while broader and weaker bands occurred near 2.230 and 2.4  $\mu\text{m}$  for heated ferricopiapite. The spectrum of jarosite includes several features that parallel the hydroxy sulfate bands (Fig. 5). The mid-IR transmittance experiment revealed elimination of the rozenite and szomolnokite bands near 1626 and 1490  $\text{cm}^{-1}$ , respectively, and formation of hydroxy sulfate bands near 2000 and 2048  $\text{cm}^{-1}$  for temperatures over 300 °C (Fig. 6).

**Implications for Mars:** Fe-rich hydroxy sulfates appear to be present on Mars [1-3] and small differences in the NIR hydroxy sulfate bands near 2.23 and 2.37-2.4  $\mu\text{m}$  can be used to identify the chemistry of these species and constrain the geochemical history.

**Acknowledgements:** Thanks are due to J.-F. Boily for the use of his lab for the transmission spectroscopy experiments and to NASA for support of RELAB for the reflectance measurements. MY appreciates support from the Swedish Research Council (VR-2018-06694) and the NPP.

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