

**QUANTIFICATION OF STRUCTURAL H<sub>2</sub>O AND TOTAL H<sub>2</sub>O CONTENTS IN IRON SULFATE MINERALS USING DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY.** B. C. Hyde<sup>1</sup> and P. L. King<sup>2,1</sup>, <sup>1</sup>Department of Earth Sciences, The University of Western Ontario, London, Ontario, N6A 5B7, Canada, <sup>2</sup>Institute of Meteoritics, The University of New Mexico, Albuquerque, New Mexico, 87131, USA.

**Introduction:** Fe-sulfates with OH<sup>-</sup> &/or H<sub>2</sub>O are found in martian meteorites [e.g. 1] & on the martian surface [e.g. 2]. These minerals may provide evidence for past surface environments & potential habitability, [e.g. 3]. Several studies have characterized Fe-sulfates using spectral features [e.g., 4-6]. However, unique identification of Fe-sulfates is hampered by the occurrence of mineral assemblages with several Fe-sulfates, inherent variations in the H contents of some Fe-sulfates (e.g. schwertmannite, Table 1) & phase transitions that may occur as a function of temperature & relative humidity [7].

To better characterize Fe-sulfates – in martian samples (meteorites or returned samples) & remotely collected data – it is necessary to quantify their H<sub>2</sub>O & OH<sup>-</sup> contents. Furthermore, if calibration factors were known for H-bearing minerals they could be used to evaluate the bulk H content of the martian surface using remotely sensed IR data. We examined laboratory biconical diffuse reflectance spectra of H-bearing Fe-sulfates to calibrate wt.% H<sub>2</sub>O & total H<sub>2</sub>O (H<sub>2</sub>O+OH<sup>-</sup>) contents using small masses of Fe-sulfates (<5 mg). We applied Kubelka-Munk (K-M) theory [e.g. 8] & the normalized optical path length (NOPL) method [9-11] because both methods may be used in either laboratory or remote sensing applications.

**Background:** K-M theory is valid when the absorption coefficient & scattering centers are small [e.g. 8] & it uses the remission function:

$$f(R_\infty) \equiv (1 - R_\infty)^2 / 2R_\infty \quad (1)$$

where  $R_\infty$  is the reflectance from an infinitely thick sample. K-M band heights vary linearly with concentration.

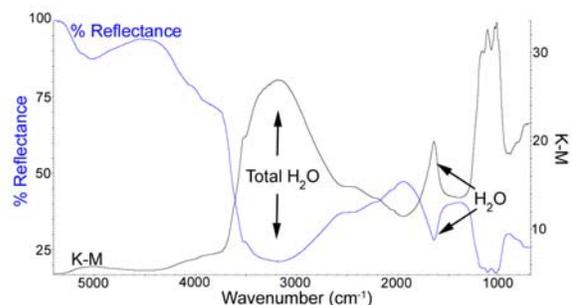
NOPL utilizes Beer's Law as an approximation for describing absorption in a reflectance spectrum. This parameter is calculated by

$$NOPL_\lambda = \ln[R(\lambda) + 1 - R_c(\lambda)] / \ln[1 - R_c(\lambda)] \quad (2)$$

Where  $R(\lambda)$  is the sample reflectance at wavelength  $\lambda$  &  $R_c(\lambda)$  is the reflectance of the continuum at  $\lambda$  [9].

**Analysis Methods:** A Nicolet Nexus 670 FT-IR with a Pike Technologies Automated Diffuse Reflectance accessory was used at the University of New Mexico (UNM) to collect biconical reflectance infrared (IR) data. An Everglo Globar source, KBr beamsplitter & DTGS detector were used to collect spectra at 4 cm<sup>-1</sup> resolution from 700 to 5400 cm<sup>-1</sup> (Fig. 1). Samples were sieved to <45 μm & diluted with KBr (verified anhydrous). An Al-coated alignment mirror was

used to collect a background before & after each analysis. We confirmed that there were no changes in the spectral features over time & a dry-air purge chamber was not used because it caused sample dehydration.



**Figure 1.** Ferricopiapite spectrum in % reflectance (scaled to max % reflectance) & K-M conversion.

Samples in this study (Table 1) were analyzed for bulk chemistry. All samples were synthesized following [12], except the natural jarosite. To calibrate H<sub>2</sub>O (1635-1650 cm<sup>-1</sup>) & total H<sub>2</sub>O (3150-3385 cm<sup>-1</sup>), we made several KBr dilutions of each sample. We can determine OH = total H<sub>2</sub>O – H<sub>2</sub>O.

Mineral	Formula
Jarosite (Jrs)	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
*Schwertmannite (Schwrt)	Fe <sup>3+</sup> <sub>8</sub> O <sub>8</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>x</sub> ·nH <sub>2</sub> O (where 1 ≤ x ≤ 1.75)
Szomolnokite (Szom)	Fe <sup>2+</sup> SO <sub>4</sub> ·1H <sub>2</sub> O
Ferricopiapite (Fcop)	Fe <sup>3+</sup> <sub>2/3</sub> Fe <sup>3+</sup> <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·20H <sub>2</sub> O
#Paracoquimbite (Pcoq)	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O

**Table 1.** Minerals in this study & ideal formulae.

\*minor goethite [Fe<sup>3+</sup>OOH], †minor rhomboclase [HFe<sup>3+</sup>(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O], #minor Fcop & rhomboclase.

The amount of H present in the Fe-sulfates was determined using mass spectrometry methods. Measured H concentrations were used to calculate concentrations of H<sub>2</sub>O & total H<sub>2</sub>O.

**Results & Discussion:** As expected, calibration curves for H<sub>2</sub>O & total H<sub>2</sub>O derived using K-M theory are linear (Fig. 2) while NOPL parameter shows calibration factors that can be fit as suggested by [9] (Fig. 3, Table 2). Our results show that Fe-sulfate mineralogy affects the calibration factors for H<sub>2</sub>O & total H<sub>2</sub>O [cf. 9]; calibrations are not independent of mineralogy.

Past work [9-11] has compared fits using  $\sigma_{res}$  (standard deviation of the residuals). The NOPL method produces better fits when viewing R<sup>2</sup> &  $\sigma_{res}$ , with the exception of szomolnokite. The NOPL calibration is

more accurate than K-M when samples contain secondary minerals (i.e. Schwrt, Fcop & Pcoq).

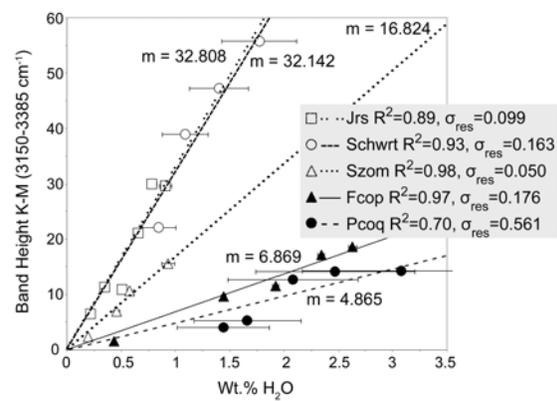
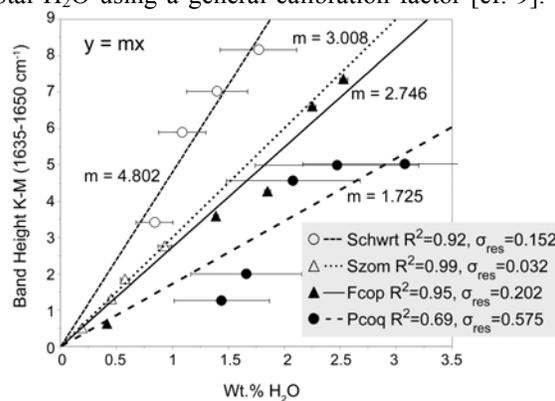
Each mineral has a calibration curve with unique fit parameters likely due to the arrangement of H<sub>2</sub>O & OH<sup>-</sup> in their structure. Fcop & Pcoq have similar calibration curves in most cases probably because both minerals contain some H<sub>2</sub>O that is structurally isolated & not coordinated with Fe or S. Szom & Jrs calibration curves are similar for the NOPL technique perhaps because they contain H<sub>2</sub>O & OH<sup>-</sup> (respectively) tightly bound in the mineral structure [13]. The structural locality of H<sub>2</sub>O & OH<sup>-</sup> is poorly understood in Schwrt.

**Conclusions:** The diffuse reflectance technique has been successfully calibrated for H<sub>2</sub>O & total H<sub>2</sub>O. K-M transformation capabilities are available with commercial software, making this method simple. NOPL allows for quantification directly from reflectance data & produces better fits. Both calibration methods are mineral dependent – it is not possible to quantify H<sub>2</sub>O & total H<sub>2</sub>O using a general calibration factor [cf. 9].

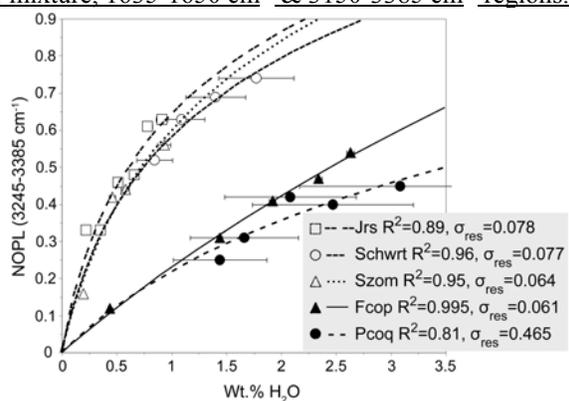
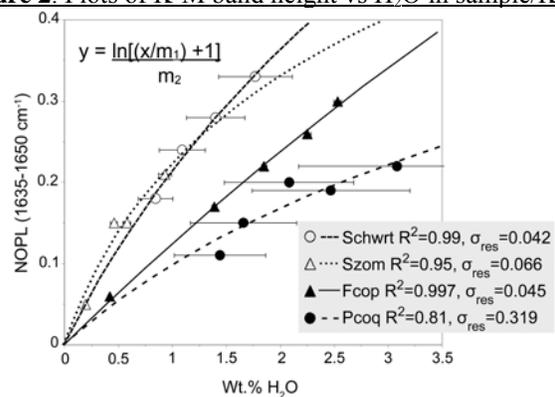
However, if the mineral ID can be determined from the spectra then quantification is possible.

**References:** [1] Wentworth S.J. & Gooding J.L. (1996) *LPS XXVII*, 1421-1422. [2] Lane M.D. et al. (2008) *Am Mineral*, 93, 728-739. [3] King P.L. & McSween H.Y. (2005) *JGR*, 110(E12), DOI: 10.1029/2005JE002482. [4] Cloutis E.A. et al. (2006) *Icarus*, 184, 121-157. [5] Lane M.D. (2007) *Am Mineral*, 92, 1-18. [6] Johnson J.R. et al. *Geophys Res Lett*, 34, DOI:10.1029/2007GL029894. [7] Chou I-M. et al. (2002) *Am Mineral*, 87, 108-114. [8] Morris R.V. et al. (1982) *Geophys Res Lett*, 9(2), 113-116. [9] Milliken R.E. & Mustard J.F. (2005) *JGR*, 110, DOI:10.1029/2005JE002534. [10] Milliken R.E. & Mustard J.F. (2007a) *Icarus*, 189, 550-573. [11] Milliken R.E. & Mustard J.F. (2007b) *Icarus*, 189, 574-588. [12] Hyde et al. (2008) *LPI Contrib.*, 1401, #4042. [13] Hawthorne, F.C. et al. (2000) *in Rev in Min & Geochem*, 40, 1-112.

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**Figure 2.** Plots of K-M band height vs H<sub>2</sub>O in sample/KBr mixture, 1635-1650 cm<sup>-1</sup> & 3150-3385 cm<sup>-1</sup> regions.



**Figure 3.** (Above) Plots of NOPL vs H<sub>2</sub>O in sample/KBr mixture, 1635-1650 cm<sup>-1</sup> & 3245-3385 cm<sup>-1</sup> regions.

Sample	1635-1650 cm <sup>-1</sup>		3245-3385 cm <sup>-1</sup>	
	m <sub>1</sub>	m <sub>2</sub>	m <sub>1</sub>	m <sub>2</sub>
Jrs	-	-	0.207	2.734
Schwrt	1.848	2.015	0.249	2.769
Szom	0.559	4.589	0.329	2.327
Fcop	9.005	0.841	4.575	0.859
Pcoq	1.903	4.255	1.275	2.644

**Table 2.** (Left) Fit parameters for Fig. 3. The fit equation is NOPL = {ln[(x/m<sub>1</sub>) + 1]}/m<sub>2</sub>.