DEHYDRATION OF FERROUS SULFATES MONITORED BY XRD – IMPLICATIONS FOR CHEMIN.

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Introduction: The Mars Science Laboratory (MSL) mission is intended to launch in 2009. Mounted internal to the rover, the CheMin instrument is a combined X-ray diffraction/X-ray fluorescence (XRD/XRF) instrument that will determine the mineralogy of soil or crushed rock presented by the surface sampling system [1]. In order to characterize sulfate minerals that are stable on Mars, we have studied the stability of a number of ferrous sulfates and carried out XRD measurements to track their stability in a controlled environment.

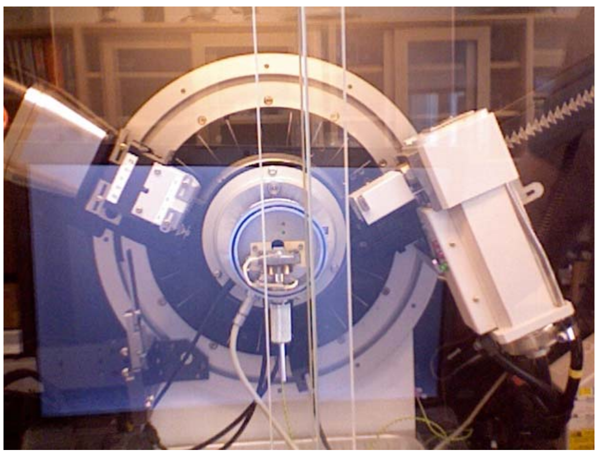

Figure 1. Bruker D-8 XRD instrument used for this investigation, showing the XRD source, TTK-450 temperature stage and Vantec detector. The sample diameter is ~1cm.

Ferrous Sulfate minerals on Mars: Fe-bearing sulfates have long been suspected as conspicuous minerals likely to be stable on Mars today [2-3]. Previous studies have investigated the stability of ferric sulfates on the premise that they are more likely to be stable on Mars than ferrous sulfates [4-5]. Given the possibility that some areas of Mars may be more reducing, particularly the shallow subsurface, we have concentrated in this study on ferrous sulfates (Table 1).

Experimental Methods: Our intention was to examine the stability of each sample as a function of temperature and time. A small amount of each sample was powdered dry with an agate mortar and pestle and placed on the TTK-450 heating stage. A rapid XRD run was carried out to determine the mineralogy of the sample in ambient conditions (23°C). Each sample was then heated in vacuum (~0.17 mbar or 110 milliTorr)

Mineral	Ideal formula
Melanterite	$Fe^{2+}SO_4\cdot 7H_2O$
Siderotil (not studied)	*$Fe^{2+}SO_4\cdot 5H_2O$*
Rozenite	$Fe^{2+}SO_4\cdot 4H_2O$
Szomolonokite	$Fe^{2+}SO_4\cdot 1H_2O$
Halotrichite	$Fe^{2+}Al_2SO_4\cdot 22H_2O$
Romerite	$Fe^{2+}{}_3(SO_4)_4\cdot 14H_2O$

Sample #	Constituents	Origin
Reagent	Rozenite	"Melanterite" reagent
136727MEL	Halotrichite + Szomolnokite	D. Dyar collection
140175	Halotrichite	White Mountains, Mono County, CA. Smithsonian collection
C-5905-2	Romerite + Szomolnokite	Cerritos Bayas, Chile Smithsonian collection
JB 626-C	Melanterite	J. Banfield collection

Table 1. Ferrous sulfate mineral formulae and samples investigated in this study.

at 50°C steps every 30 minutes, and another XRD measurement was made at each step to monitor the mineral stability. XRD measurements were analyzed by Rietveld refinement using GSAS [6].

Observations: *Reagent.* This pelletized sample, was labeled 'Melanterite Reagent', was actually rozenite under ambient conditions. Temperature-resolved XRD measurements show that rozenite broke down to an amorphous form between 50-100°C. Measurements on another sample with 10°C/30 min increments showed that it began to break down at 70°C and was completely amorphous by 90°C (Figure 2).

136727MEL. XRD measurements in ambient conditions identified halotrichite and szomolnokite in this

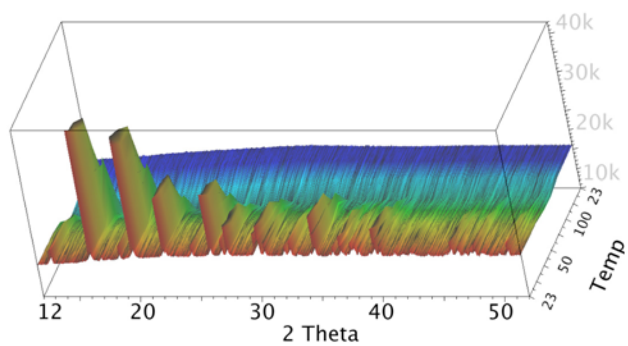

Figure 2. Rozenite sample heated from 23 to 100 and back down to 23°C in 10°C steps.

sample. XRD measurements to 300°C in 50°C increments showed that halotrichite broke down, begining at 50°C and completely by 150°C. Szomolnokite remained after this heating procedure and was not altered during heating to 300°C.

140175. Ambient XRD runs identified halotrichite in this sample, which was heated under vacuum from 23 to 150°C in 10°C increments and back down to 23°C in one step. Halotrichite progressively broke down above 40°C and was completely gone by ~100°C. No high-temperature phases formed and no new phases formed upon cooling to 23°C.

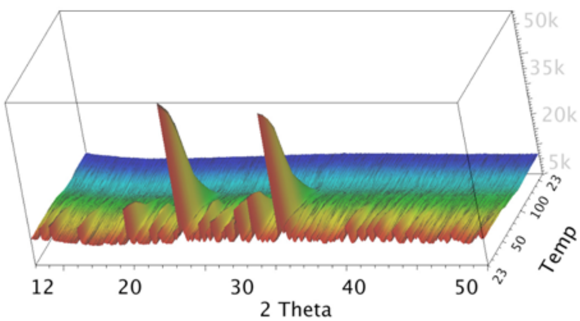

Figure 3. Halotrichite sample heated 23-100-23°C

C-5905-2. This red-crusted sample (Figure 4) was dissected to separate crust from base. The base was identified as szomolnokite, and heating to 300°C did not modify the szomolonokite. The crust consisted of römerite, which broke down between 50 and 100°C (Figure 5).

Figure 4. Sample C-5902-2 being prepared. The red crust is römerite and the grey material is szomolnokite.

JB626-C. A pick was used to separate a portion of this small sample, which had been sealed inside a capped plastic tube. Measurements under ambient conditions (22.5C, RH~49%) showed it to be melanterite. This was unexpected as previous research suggested that melanterite is unstable in these conditions [7]. After 15 hours of exposure to ambient conditions (22.5C, RH~49%), there was no change to the melanterite XRD pattern. On exposure to vacuum, melanterite broke down immediately to an amorphous phase (Figure 6).

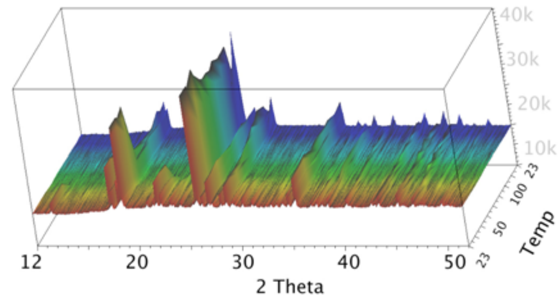

Fig. 5. Römerite/szomolnokite sample heated 23-100-23°C

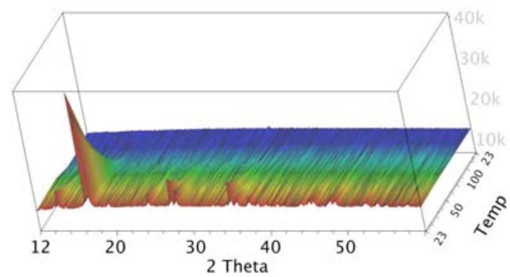

Figure 6. Melanterite sample heated 23-100-23°C

Implications for CHEMIN: The results of our investigation suggest: 1) Melanterite is stable only under ambient conditions and breaks down to an amorphous form in a vacuum; 2) Rozenite breaks down to an amorphous phase when heated under vacuum above 70°C; 3) Römerite breaks down to an amorphous phase above 50°C; 4) Halotrichite breaks down to an amorphous phase when heated above 40-50°C; and 5) Szomolnokite is stable *in vacuo* under heating to 300°C. This study suggests that under current conditions on Mars, melanterite may be unstable. Szmolnokite, rozenite, römerite and halotrichite are likely to be stable under Martian conditions, although potentially elevated temperatures with the CheMin instrument, up to 50°C, may render römerite and halotrichite amorphous.

References: [1] Blake, D.F. et al, (2005) *LPSC XXXVI*, #1608. [2] Burns, R.G., (1987) *JGR 92, E570-E574*, [3] Bish, D.L., et al, (2003) *Icarus*, 164, 96-103. [4] Vaniman, D.T., et al, (2004) *Nature*, 431, 663-665. [5] Hasenmueller, E.A. and Bish, D.L. *LPSC XXXVI* #1164 [6] Larson, A.C. and Von Dreele, R.B. (2000) *LANL Report* LAUR 86-748. [7] Peterson, R.C. and Grant, A.H. (2005) *Can. Mineral.*, 43, 1301-1311

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