

Mars surface mineralogy: Kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Characterization of a terrestrial end-member J.J. Papike¹, J.M. Karner¹, P.V. Burger¹, C.K. Shearer¹, and A. Wang² ¹Institute of Meteoritics, Univ. of New Mexico, Albuquerque, NM 87131; jpapike@unm.edu; ²Dept. Of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington Univ., St. Louis, MO 63130

Introduction. Previous missions to Mars have shown that the element sulfur and the sulfate minerals are important constituents of the martian regolith and bedrock. Both sulfates and sheet silicates, including several clay minerals, have been identified by spectral instruments such as OMEGA and CRISM. The mid-infrared emission spectroscopy of sulfates is reviewed by Lane [1] and the Raman spectral characteristics of the magnesium sulfate hydrates are reviewed by Wang et al. [2]. The experimental stability of magnesium sulfate hydrates is reviewed by Chipera and Vaniman [3]. The focus of this paper is on the magnesium sulfate hydrate, kieserite, because it has been positively identified as an important sulfate mineral on Mars. The sulfate polyhydrates of magnesium have OH related absorptions in the NIR but they are less distinct from each other than kieserite, perhaps due to their weaker hydrogen bonding. Kieserite has a 2.4 micron band that is shifted toward longer wavelengths presumably because of its stronger hydrogen bonding (Greg Swayze, 2007, personal communication). As such, kieserite has a high spectral contrast compared to other polyhydrates so it is more easily detected based on the unique wavelength position of the 2.4 micron band and its relatively greater intensity. Also, recent studies by Chipera and Vaniman [3] show that kieserite, once crystallized, is more resilient than the other Mg sulfate hydrates so it can remain metastable for long periods of time in the dry, cold, martian regolith. Papike et al. [4] reviews the crystal chemistry of the kieserite group of minerals (see Figure 1). The kieserite structure is a type of framework structure where chains of corner-sharing octahedra (blue) are cross-linked by sulfate tetrahedra (yellow). The oxygen ligands (O1 and O2) connect octahedra and tetrahedra. The important oxygen ligand, O3, bridges between two octahedral and forms two strong hydrogen bonds (hydrogen in red). These are the bonds that give rise to the distinctive spectral signature of kieserite. Figure 1 shows the structure down the b axis. Both the sulfate tetrahedra and O3 oxygen sit on two-fold axes that run parallel to b. In this projection the H-O-H bond linkage appears collinear but it is not (see Papike et al. [4]).

Here we characterize a terrestrial end-member of kieserite from Lehrte, Niedersachsen (Lower Saxony), Germany, kindly provided by the Smithsonian Institution. This sample appears to be from Permian evaporates in the Hansa mine area.

The Stassfurt bed consists mostly of kieserite, sylvite-halite assemblage.

Results and Discussion.

RAMAN SPECTRAL ANALYSIS. The identification, based on the Raman spectra from several loose grains of Smithsonian sample, suggests kieserite with minor amounts of pentahydrate attached at a few locations on the grain surfaces. In an experimental study on the stability fields of Mg-sulfates, Wang [2] found two types of “kieserite”, i.e, the two types have different XRD patterns and different Raman spectra. For example, Figure 2 shows two types of Raman spectra in the H-O-H stretching vibration region. The Smithsonian kieserite has a spectrum similar to that of “kieserite-wet”, having a doublet in this spectral region. In Wang’s experiments, the “kieserite-wet” phase is stable at 50.9% relative humidity at 50°C after more than 2500 hrs.

EMP ANALYSES. We report electron microprobe analyses in Table 1. We used the same techniques described by Papike et al. [5] but with a 30 micron beam to avoid (as much as possible) volatile loss. We did traverses across several large chips and the results show that the majority of the sample is nearly stoichiometric kieserite. The average hydrogen (atoms per formula unit) we estimate by difference is 2.17, which is slightly more than 1 H_2O per formula unit, but consistent with Wang’s “wet kieserite” interpretation.

INAA ANALYSIS. The INAA analysis was conducted by Randy Korotev at Washington Univ., St. Louis. Table 2 reports the results and shows that the sample is very near an end-member composition. Clearly there is very little solid solution toward other members of the kieserite group (Fe^{2+} , Zn, Ni, Co). This makes the sample ideal for use as standard for techniques that require end-member compositions. Lane [1] used this sample for her mid-infrared emission spectroscopy study of sulfates. However, she referred to it in her Table 1 as hexahydrate with the note (likely kieserite).

References.

- [1] Lane (2007) *Am. Min.*, 92, 1-18. [2] Wang et al. (2006) *GCA*, 70, 6118-6135. [3] Chipera and Vaniman (2007) *GCA*, 71, 241-250. [4] Papike et al. (2007) 7th Intl. Conf. on Mars, #3004. [5] Papike et al. (2006) *Am. Min.*, 91, 1197-1200.

Figure 1.

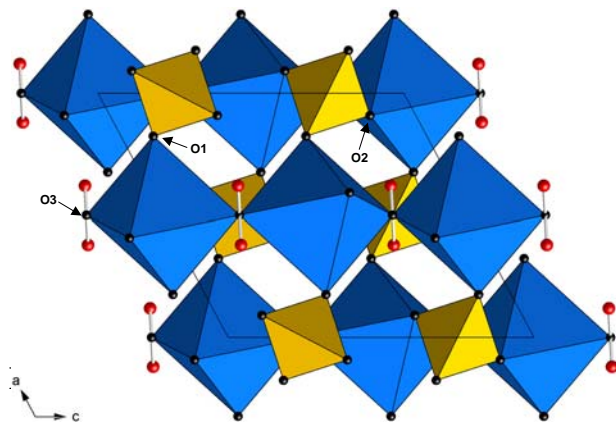


Figure 2.

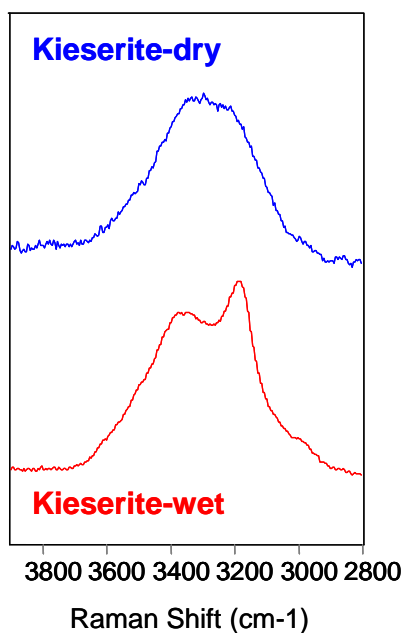


Table 1. Representative analyses for kieselite from Lehrte, Niedersachsen, Germany.

	1-1	1-7	2-5	Average N = 19
CoO	0.03	0.10	0.00	0.03
SO ₃	56.6	56.8	56.7	56.5
Na ₂ O	b.d.	b.d.	b.d.	b.d.
V ₂ O ₃	b.d.	b.d.	b.d.	b.d.
K ₂ O	b.d.	b.d.	b.d.	b.d.
MoO ₃	b.d.	b.d.	b.d.	b.d.
MgO	29.6	29.2	29.2	29.2
Fe ₂ O ₃	b.d.	b.d.	b.d.	b.d.
CaO	b.d.	b.d.	b.d.	b.d.
Al ₂ O ₃	b.d.	b.d.	b.d.	b.d.
NiO	b.d.	b.d.	b.d.	b.d.
H ₂ O*	13.7	13.9	14.0	14.2
Total	100	100	100	100

Cations based on 5 oxygen atoms

Co	0.00	0.00	0.00	0.00
S	0.98	0.98	0.98	0.97
Na	0.00	0.00	0.00	0.00
V	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00
Mo	0.00	0.00	0.00	0.00
Mg	1.02	1.00	1.00	1.00
Fe	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00
H	2.11	2.12	2.15	2.17
Total	4.10	4.10	4.12	4.14

b.d. = below detection, *Calculated by difference to 100% sum.

Table 2. Results from Instrumental Neutron Activation Analysis on kieselite from Lehrte, Niedersachsen, Germany.

Na ₂ O	0.0097	wt.%
K ₂ O	0.033	wt.%
CaO	<0.017	wt.%
Sc	0.0779	ppm
Cr	<0.09	ppm
FeO	0.00058	wt.%
Co	0.0065	ppm
Ni	<0.9	ppm
Zn	0.34	ppm
As	0.16	ppm
Br	55	ppm
Rb	0.47	ppm
Sr	<2.5	ppm
Zr	<1.3	ppm
Sb	0.0051	ppm
Cs	0.0255	ppm
Ba	<4	ppm
La	<0.0018	ppm
Ce	<0.06	ppm
Nd	<0.4	ppm
Sm	<0.0012	ppm
Eu	<0.0005	ppm
Tb	<0.0016	ppm
Yb	<0.005	ppm
Lu	<0.0007	ppm
Hf	<0.0007	ppm
Ta	<0.001	ppm
W	<0.25	ppm
Th	<0.005	ppm
U	<0.024	ppm