

CRYSTAL STRUCTURE OF A NEW $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$ HYDRATE PHASE MEASURED UNDER MARS-RELEVANT CONDITIONS. K. M. Leftwich¹, D. L. Bish¹, and C. H. Chen² ¹Department of Geological Sciences, Indiana University, Bloomington, IN 47405, kmleftwi@indiana.edu; ²Indiana University Molecular Structure Center, Indiana University, Bloomington, IN 47405.

Introduction: Sulfate minerals are of particular interest on Mars' surface due to the ability of many to hydrate and dehydrate reversibly. The Mg-sulfate system is an excellent example of such behavior, and several minerals in this system hydrate and dehydrate. Meridianiite, $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, occurs only below 2°C [1] and readily dehydrates above that temperature to a less-hydrated MgSO_4 -hydrate (e.g., epsomite or hexahydrate) and (re)hydrates upon exposure to low temperatures. This behavior suggests that phases in this system and in other similar systems are potential sources and repositories for H_2O on the surface of Mars. This study examines the behavior of the sodium magnesium sulfate-hydrate system, predicted to occur on Mars by Clark *et al.* (1981) based on the concentration of Mg observed by X-ray fluorescence (XRF) analyses on the Viking lander [2]. King *et al.* (2004) also predicted phases in this system based on groundwater compositions of igneous rocks on Earth [3]. This system was examined under Mars-relevant conditions to determine the potential for phases in the system to participate in the martian H_2O cycle.

A natural sample of blödite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) from Soda Lake, CA was exposed to low temperatures ($T \leq -10^\circ\text{C}$) for powder XRD experiments. The investigations of this mineral system at Mars-relevant RH/T conditions produced X-ray diffraction patterns that indicated a change in mineralogy at temperatures $\leq -10^\circ\text{C}$ [4]. The peaks measured at low temperature did not correspond to those of any previously known phase or combination of phases, which led to the conclusion that the peaks represented a new member of the $\text{Na}_2\text{Mg}(\text{SO}_4)_2\text{-H}_2\text{O}$ system. Attempts at solving the crystal structure of this material using powder XRD data were not successful. We subsequently prepared a small single crystal of the low-temperature phase. A deliquesced sample of powdered blödite was held in a -10°C freezer for a week, during which time crystals of the new phase formed.

Single-Crystal Diffraction Methods: Data used in determination of the structure of the low-temperature

phase were obtained using a Bruker ApexII diffractometer (Mo radiation: $\lambda=0.7107\text{\AA}$) at the Indiana University Molecular Structure Center (IUMSC). Data were collected while the crystal was under a nitrogen cold stream at -123°C . Apex2 software [5] and Oxford Crystals [6] were used in the determination of the crystal structure of the 16-hydrate phase. An $\sim 0.5 \times 0.2 \times 0.1$ mm crystal was mounted onto a MiTeGen micromount and held under the cold stream. Although the RH during the single-crystal experiment is unknown, it is likely to have been high, and the fact that the crystal remained hydrated supports this assumption.

Results: The single-crystal data were analyzed using the charge-flipping method with Oxford Crystals [6]. Table 1 shows the unit-cell parameters of the monoclinic ($P\bar{1}$) structure and atom positions from the single-crystal structure solution. This structure was determined using 2,537 reflections (GoF=1.00 and $R=3.91\%$). A stoichiometry of $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ was assumed, and all Na and Mg cations and sulfate tetrahedra were identified. H_2O molecules were assigned to unidentified electron density on difference-Fourier maps, yielding a formula of $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$. Figure 1 shows the crystal structure (produced in XtalDraw [7]); Mg atoms (green octahedra) and sodium atoms (blue octahedra) are octahedrally coordinated by H_2O molecules, creating "sheets" of cations. Between these sheets are independent sulfate tetrahedra (blue) with alternating

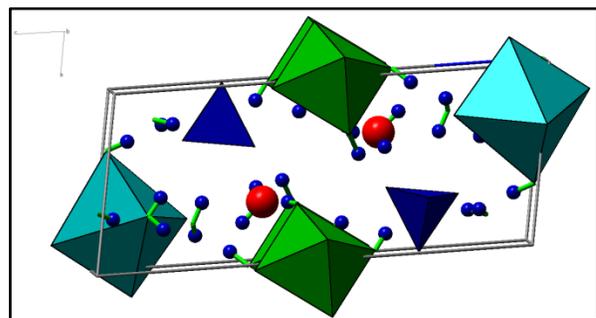


Figure 1. Crystal structure of $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 16\text{H}_2\text{O}$ (XtalDraw [7]).

up/down orientations along the b axis. The remaining H_2O molecules in the unit cell are situated with their hydrogen ions oriented toward apical oxygens of the sulfate tetrahedra.

a (Å)	6.5590(12)	α (°)	87.456(15)
b (Å)	6.6277(14)	β (°)	79.682(15)
c (Å)	14.441(3)	γ (°)	65.847(13)
Atom	x	y	z
S	0.23890(9)	0.39252(9)	0.74474(4)
Mg	1.0	0.0	0.5
Na	0.75164(15)	0.05172(15)	0.95007(6)
O1	0.2977(3)	0.1529(3)	0.75328(11)
O2	0.3642(3)	0.4301(3)	0.65497(11)
O3	0.9920(3)	0.5100(3)	0.74628(11)
O4	0.3006(3)	0.4748(3)	0.82425(11)
O5	0.6788(3)	0.0258(3)	0.55340(13)
O6	0.0305(3)	0.0495(3)	0.63751(12)
O7	0.1213(3)	0.6680(3)	0.52016(13)
O8	0.7067(3)	0.4079(3)	0.88619(12)
O9	0.6672(3)	0.7492(3)	0.00492(13)
O10	0.8388(3)	0.0939(3)	0.10014(12)
O11	0.7485(3)	0.9612(3)	0.78981(12)
O12	0.6653(3)	0.6360(3)	0.62901(13)
H1	0.712(6)	0.667(6)	0.050(3)
H2	0.636(7)	0.999(6)	0.774(3)
H3	0.181(7)	0.634(6)	0.563(3)
H4	0.809(6)	0.019(6)	0.142(3)
H5	0.568(7)	0.142(7)	0.580(3)
H6	0.609(7)	0.429(6)	0.862(3)
H7	0.704(7)	0.658(7)	0.971(3)
H8	0.119(7)	0.059(7)	0.658(3)
H9	0.583(7)	0.600(7)	0.646(3)
H10	0.668(7)	0.931(7)	0.574(3)
H11	0.946(7)	0.036(6)	0.684(3)
H12	0.787(7)	0.401(7)	0.848(3)
H13	0.183(7)	0.584(7)	0.476(3)
H14	0.820(7)	0.820(7)	0.780(2)
H15	0.805(7)	0.191(7)	0.119(3)
H16	0.7740	0.5915	0.6698

Discussion: The RH/T conditions under which the 16-hydrate was observed indicate that this phase will be stable on the surface of Mars, given an assemblage containing $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ phases. Mars Curiosity REMS (Rover Environmental Monitoring Station) data have shown diurnal ground temperature readings varying between 3°C and -91°C [8]. These temperatures encompass the experimental stability fields of both blödite and the 16-hydrate [4]. Phoenix lander soil temperature data from the Thermal and Electrical Conductivity Probe (TECP) returned values of -19°C to -92°C [9], suggesting that the 16-hydrate is likely to be the stable $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ hydrate phase in polar regions of Mars.

Acknowledgements: Support from a NASA Mars Fundamental Research Grant is gratefully acknowledged.

References: [1] Peterson R.C. et al. (2007) *Am. Min.*, 92, 1756-1759. [2] Clark B.C. et al. (1981) *Icarus*, 45, 370-378. [3] King P.L. et al. (2004) *Geoch. Cosmoch. Acta*, 68.23, 4993-5008. [4] Leftwich K.M. and Bish D.L. (2013) *LPS XLIV*. [5] Bruker (2007) *Apex2*. [6] Betteridge P.W. et al. (2003) *J. Appl. Cryst.*, 36, 1487. [7] Downs R. et al. XtalDraw Version Aug 1, 2003. [8] marsweather.com/data. [9] Zent A.P. et al. (2010) *JGR*, 115, E00E14.