American Mineralogist, Volume 94, pages 1005–1011, 2009

The crystal structure and hydrogen bonding of synthetic konyaite, $Na_2Mg(SO_4)_2 \cdot 5H_2O$

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Abstract

The crystal structure of synthetic konyaite, $Na_2Mg(SO_4)_2 \cdot 5H_2O$, $a = 5.7690(8)$, $b = 23.951(3)$, $c = 8.0460(11)$ Å, $\beta = 95.425(2)°$, $V = 1106.8(3)$ Å^3, space group $P2_1/c$, $Z = 4$, was solved using single-crystal X-ray diffraction. Hydrogen atom positions were determined and the structure solution was refined to $R_1 = 3.31\%$ and $wR_2 = 6.28\%$ for the 2167 measured independent reflections. Three distinct cation sites host the Mg and Na atoms in distorted octahedra and eight-coordinated polyhedra. The coordination polyhedra share edges to form compact sheets oriented perpendicular to *b* and linked to one another by hydrogen bonds. This results in a {010} tabular habit. A comparison of this structure is made to that of blödite [$Na_2Mg(SO_4)_2 \cdot 4H_2O$], the dehydration product of konyaite. Konyaite is discussed within the context of the Na_2O-MgO-SO_4-H_2O system. This study is part of ongoing investigations into the dehydration mechanisms and phase stability of this system.

Keywords: Konyaite, crystal structure, single-crystal X-ray diffraction, hydrogen bonding, blödite, dehydration, phase stability

Introduction

Konyaite is a hydrated sodium-magnesium-sulfate salt. It is most commonly found as white mineral efflorescences associated with marine and lacustrine sediments such as those found in the Great Konya Basin, Turkey (van Doesburg et al. 1982), and in the Northern Great Plains of North Dakota (Keller et al. 1986a). Konyaite is sensitive to variations in temperature and humidity and dehydrates readily to blödite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$. Both phases precipitate when saline solutions become supersaturated through evaporation (Keller et al. 1986b).

The Na_2O-MgO-SO_4-H_2O system has been the subject of numerous studies. Archibald and Gale (1924) and Blasdale and Robson (1928) both concerned themselves with mapping out the phase relationships, but neither study identified konyaite. D'Ans (1933) later suggested that a metastable phase may exist in the blödite field of stability, describing it as a labile double salt, but this was not further investigated. The study of individual phases related to this system also became important: Rumanova (1958) solved the crystal structure of blödite, later to be refined by Hawthorne (1985). Baur (1964) investigated the crystal structure of epsomite ($MgSO_4 \cdot 7H_2O$), while Zalkin et al. (1964) studied hexahydrite ($MgSO_4 \cdot 6H_2O$) and Fischer and Hellner (1964) studied vanthoffite, $Na_6Mg(SO_4)_4$. Fang and Robinson (1970) also described the structure of löweite, $Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O$. Figure 1 shows how these phases are compositionally related to one another, and to thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4 \cdot 10H_2O$). Driessen and Schoorl (1973) tied the previously modeled phase stability relationships to a field study of the saline soils of the Great Konya Basin, but konyaite was again overlooked. Meanwhile, Nord (1973) and later Hawthorne and Ferguson (1975) investigated the structure of thenardite. Friedel (1976) found that a salt with the formula $Na_2Mg(SO_4)_2 \cdot 5H_2O$ was often found in saline soil crusts, and that although it altered to blödite when allowed to react with its saturated solution, it persisted in dry crusts. Optical, chemical, and X-ray diffraction data were collected, but a unit cell was never refined. Subsequently, the crystal structure of mirabilite was solved by Levy and Lisensky (1978). Van Doesburg et al. (1982) described konyaite, which was recognized by the IMA as a mineral species, during a study of the salt mineralogy of the Great Konya Basin in Turkey. However, its crystal structure remained unsolved.

Numerous studies have, since then, identified konyaite as an important phase in saline soils (Shayan and Lancucki 1984; Timpson et al. 1986; Zielinski et al. 2001). Konyaite was also found to be the most common phase in mineral assemblages sampled in North Dakota by Keller et al. (1986a). Little is

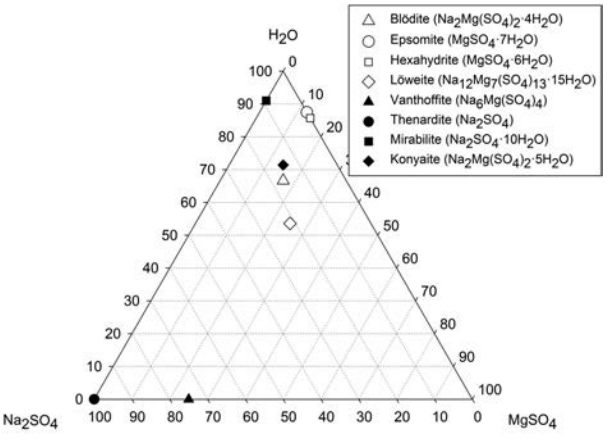

Figure 1. Selected phases of the Na_2O-MgO-SO_4-H_2O system, by mole percent (mol%) composition. Epsomite dehydrates to hexahydrite; konyaite dehydrates to blödite, and mirabilite is similarly related to thenardite. Löweite forms at higher temperatures than konyaite.

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known about the field of stability of konyaite; Keller et al. (1986a) reported having found konyaite between 6.3 and 37.9 °C, but no relative humidity constraints were provided. They suggested however, as Shayan and Lancucki (1984) did before them, that konyaite typically forms in nature and dehydrates to form blödite, and that although direct formation of blödite is possible, the required conditions for its formation do not occur as frequently as those required for konyaite. Its status as a metastable phase (van Doesburg et al. 1982; Friedel 1976) has also been questioned by Timpson et al. (1986), although its soluble nature and sensitivity to relative humidity changes make it subject to remobilization into the local watershed. Whittig et al. (1982) and Zielinski et al. (2001) have both identified konyaite as an important source of contaminants in soils, surface water, and shallow groundwater.

The behavior of konyaite and the other phases of the Na_2O-MgO-SO_4-H_2O system is partially dictated by their hydrogen-bonding arrangements, and consequently the modeling of their crystal structures has been the subject of several studies (as presented above), with the exception of konyaite. This study therefore presents the first structure solution for konyaite using single-crystal X-ray diffraction and compares it with that of blödite, its dehydration product.

Synthesis, diffraction experiments, and refinement

Synthesis

The konyaite crystal used in this study was synthesized following the method described by van Doesburg et al. (1982). Approximately 50 mL of a solution with a 1:1 molar ratio of $MgSO_4$ and Na_2SO_4 was prepared and evaporated at 27 °C and 79% relative humidity (RH) in a large Petri dish with a perforated cover to allow evaporative concentration. Crystals as large as 0.30 × 0.10 × 0.06 mm were obtained after ~72 h. These synthetic konyaite crystals are soft (H = 2.5), elongate, colorless to white, translucent to transparent, and exhibit a {010} tabular habit. They were also found to commonly form radiating masses (this study; van Doesburg et al. 1982).

Diffraction experiments

X-ray powder diffraction data of the synthesized material was produced using a PANalytical X'Pert Pro θ-θ diffractometer, and collected with an X'Celerator position-sensitive detector. Cobalt radiation (1.7903 Å) was used at a setting of 45 kV and 40 mA to collect data over a range of 5 to 70 °2θ. The pattern identification was carried out using the X'Pert Highscore software, and the ICDD database to verify that the synthesized crystals were indeed konyaite. The collected pattern intensities are shown in Table 1. An equant single-crystal fragment was selected, immersed in mineral oil to prevent dehydration, and inserted in a 0.3 mm glass capillary. The prepared crystal was then mounted on a Bruker SMART APEX II X-ray diffractometer and studied using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over a 2θ range of 3.40 to 52.00°. The sample was cooled to 180 K using a nitrogen gas Cryostream Controller 700 during data collection. Table 2 compares the unit cell of konyaite determined here with those determined by van Doesburg et al. (1982).

Refinement

A total of 2167 (R_{int} = 0.0329) independent reflections were collected, and a multi-scan approach was used to correct for X-ray absorption. Table 3 presents crystal data and refinement parameters. Intensity data were processed with the Bruker AXS Crystal Structure Analysis Package (Bruker 2006). Both structure solution and refinement were performed using the SHELXTL program (v. 6.14) (Sheldrick 2008). Scattering factors were taken from Cromer and Waber (1974). Space group $P2_1/c$ was determined, based on the systematic absences. The structure was solved by direct methods and refined using a full-matrix least-squares approach. The resulting CIF[1] has been deposited.

Results and discussion

The successful refinement produced the atom coordinates and displacement parameters presented in Tables 4 and 5. Approximate hydrogen positions were found from difference-Fourier maps, and all other atom positions were determined from structure solution. Selected bond lengths and angles are listed in Table 6, and Table 7 shows information relating to hydrogen

Table 1. Strongest X-ray powder diffraction lines for konyaite

	ICDD no. 35-0649*		This study		This study	
hkl	*d* (Å)	*I* (%)	*d* (Å)	*I* (%)	d_{calc} (Å)	I_{calc} (%)
020	12.010	100	12.012	23	11.976	100
041	4.807	12	4.763	6	4.796	18
$\bar{1}21$	4.546	55	4.502	16	4.528	82
111	4.410	10	4.371	43	4.396	17
121	4.203	20	4.311	16	4.189	23
$\bar{1}31$	4.184	20	4.169	41	4.171	31
060	4.002	70	3.975	100	3.992	67
012	3.961	14	3.929	54	3.950	24
141	3.589	10	3.569	19	3.583	14
$\bar{1}12$	3.416	10	3.393	6	3.406	13
$\bar{1}42$	2.989	12	2.973	17	2.984	15
081	2.811	14	2.822	7	2.804	13
$\bar{1}52$	2.802	12	2.799	11	2.795	15
171	2.725	14	2.714	20	2.717	22
180	2.661	12	2.651	31	2.655	18
$\bar{2}31$	2.639	14	2.628	44	2.632	19
240	2.598	16	2.588	21	2.589	25
082	2.403	10	2.395	4	2.398	14
053	2.336	10	2.331	19	2.332	13

Note: The values for d_{calc} and I_{calc} were calculated from a simulated X-ray powder diffraction pattern generated from the single-crystal analysis data.
* Deposited by Keller and McCarthy (1984).

Table 2. Unit-cell data for konyaite at 180 K

	Synthetic*	Synthetic†	Natural†	Synthetic‡
a (Å)	5.79(1)	5.784(3)	5.784(3)	5.7690(8)
b (Å)	24.04(2)	24.026(9)	24.029(9)	23.951(3)
c (Å)	8.07(1)	8.066(3)	8.060(3)	8.0460(11)
β (°)	95.4(2)	95.37(3)	95.38(3)	95.425(2)
V (Å^3)	1118(2)	1116.0(5)	1115.7(5)	1106.8(3)

* From single-crystal techniques (van Doesburg et al. 1982).
† From refinement of X-ray powder diffraction data (van Doesburg et al. 1982).
‡ From single-crystal techniques at 180 K (this study).

[1] Deposit item AM-09-032, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 3. Summary of crystal data and structure refinement for konyaite

Formula	$Na_2Mg(SO_4)_2{\cdot}5H_2O$
Crystal size (mm)	0.30 × 0.10 × 0.06
Space group	$P2_1/c$ (no. 14)
a (Å)	5.7690(8)
b (Å)	23.951(3)
c (Å)	8.0460(11)
β (°)	95.425(2)
V (Å³)	1106.8(3)
Z	4
ρ (calc) (g/cm³)	2.115
λ (Å)	0.71073
μ (mm^{-1})	0.683
Temperature (K)	180(2)
θ range for data collection	1.70 to 26.00°
No. of reflections collected	11033
No. of independent reflections	2167
No. of reflections with $I > 2\sigma(I)$	1828
No. of parameters refined	203
R_{int}	0.0329
Final *R* factors [$I > 2\sigma(I)$]	$R_1 = 0.0244$, $wR_2 = 0.0585$
Final *R* factors (all data)	$R_1 = 0.0331$, $wR_2 = 0.0628$
Goodness-of-fit	1.040

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.99P]$; and $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3)$.

TABLE 4. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for konyaite

Atom	*x*	*y*	*z*	U_{eq}
Mg	0.5349(1)	0.6408(1)	0.8182(1)	0.010(1)
Na1	0.2203(2)	0.5495(1)	0.5513(1)	0.016(1)
Na2	0.1837(2)	0.4453(1)	0.8445(1)	0.017(1)
S1	0.2878(1)	0.4911(1)	0.2009(1)	0.009(1)
S2	0.0047(1)	0.6677(1)	0.3255(1)	0.011(1)
O1	–0.0458(2)	0.6177(1)	0.4224(2)	0.017(1)
O2	0.0538(3)	0.6495(1)	0.1567(2)	0.018(1)
O3	–0.1972(3)	0.7055(1)	0.3113(2)	0.016(1)
O4	0.2114(2)	0.6969(1)	0.4066(2)	0.016(1)
O5	0.1067(3)	0.4956(1)	0.3174(2)	0.016(1)
O6	0.2264(3)	0.5270(1)	0.0562(2)	0.017(1)
O7	0.2935(2)	0.4325(1)	0.1386(2)	0.013(1)
O8	0.5153(2)	0.5067(1)	0.2860(2)	0.016(1)
Ow1	0.2162(3)	0.6019(1)	0.8060(2)	0.013(1)
Ow2	0.5383(3)	0.6245(1)	0.5616(2)	0.015(1)
Ow3	0.8470(3)	0.6825(1)	0.8560(2)	0.014(1)
Ow4	0.5039(3)	0.6514(1)	1.0720(2)	0.021(1)
Ow5	0.3687(3)	0.7133(1)	0.7400(2)	0.017(1)
H1A	0.107(5)	0.622(1)	0.802(3)	0.028(8)
H1B	0.207(5)	0.582(1)	0.872(4)	0.033(9)
H2A	0.471(6)	0.648(1)	0.503(4)	0.04(1)
H2B	0.669(5)	0.622(1)	0.524(4)	0.033(8)
H3A	0.909(5)	0.680(1)	0.944(4)	0.016(7)
H3B	0.839(5)	0.718(1)	0.844(4)	0.042(9)
H4A	0.574(5)	0.675(1)	1.138(4)	0.031(8)
H4B	0.374(5)	0.650(1)	1.106(4)	0.031(8)
H5A	0.324(5)	0.739(1)	0.792(4)	0.024(8)
H5B	0.301(6)	0.715(2)	0.651(5)	0.06(1)

Note: U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Anisotropic displacement parameters (Å²) for konyaite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg	0.010(1)	0.010(1)	0.010(1)	0.000(1)	0.000(1)	0.000(1)
Na1	0.019(1)	0.015(1)	0.014(1)	–0.001(1)	–0.004(1)	–0.001(1)
Na2	0.020(1)	0.016(1)	0.014(1)	0.001(1)	0.000(1)	–0.001(1)
S1	0.010(1)	0.010(1)	0.009(1)	0.000(1)	0.000(1)	0.000(1)
S2	0.010(1)	0.010(1)	0.011(1)	0.001(1)	0.000(1)	0.000(1)
O1	0.015(1)	0.014(1)	0.024(1)	0.006(1)	0.004(1)	0.000(1)
O2	0.016(1)	0.027(1)	0.012(1)	–0.003(1)	0.000(1)	0.003(1)
O3	0.015(1)	0.013(1)	0.021(1)	–0.002(1)	–0.002(1)	0.004(1)
O4	0.016(1)	0.016(1)	0.016(1)	0.002(1)	–0.005(1)	–0.005(1)
O5	0.015(1)	0.017(1)	0.015(1)	–0.004(1)	0.004(1)	–0.002(1)
O6	0.021(1)	0.014(1)	0.015(1)	0.005(1)	–0.002(1)	0.000(1)
O7	0.015(1)	0.011(1)	0.014(1)	–0.001(1)	–0.001(1)	0.002(1)
O8	0.013(1)	0.016(1)	0.017(1)	–0.001(1)	–0.003(1)	–0.002(1)
Ow1	0.011(1)	0.013(1)	0.014(1)	0.003(1)	0.002(1)	0.001(1)
Ow2	0.014(1)	0.018(1)	0.012(1)	0.002(1)	0.003(1)	0.003(1)
Ow3	0.014(1)	0.013(1)	0.015(1)	0.002(1)	–0.002(1)	–0.002(1)
Ow4	0.014(1)	0.034(1)	0.015(1)	–0.010(1)	0.005(1)	–0.009(1)
Ow5	0.021(1)	0.013(1)	0.016(1)	–0.002(1)	–0.002(1)	0.006(1)

Note: Anisotropic parameter exponents take the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$.

TABLE 6. Selected bond lengths and angles for konyaite

Bond	Å	Angle	Deg (°)	Angle	Deg (°)
Octahedral coordination around Mg and Na1 (distorted)					
Mg-O7″	2.029(2)	Ow3-Mg-Ow2	98.41(7)	Ow1-Mg-Ow4	86.72(7)
Mg-Ow1	2.055(2)	Ow5-Mg-Ow2	84.48(8)	O7″-Mg-Ow4	91.31(7)
Mg-Ow2	2.103(2)	Ow1-Mg-Ow2	87.72(7)	Ow3-Mg-O7″	89.37(7)
Mg-Ow3	2.057(2)	O7″-Mg-Ow2	87.60(7)	Ow1-Mg-O7″	92.06(7)
Mg-Ow4	2.083(2)	Ow3-Mg-Ow4	87.18(7)	Ow3-Mg-Ow5	90.62(7)
Mg-Ow5	2.054(2)	Ow5-Mg-Ow4	96.69(8)	Ow1-Mg-Ow5	88.80(7)
Mean	2.064				
Na1-O1	2.409(2)	O1-Na1-O5′	89.97(6)	O8′-Na1-O5	104.66(6)
Na1-O5	2.324(2)	O1-Na1-Ow2	87.90(6)	Ow2-Na1-O5	124.11(6)
Na1-O5′	2.493(2)	O1-Na1-O5	84.75(6)	O1-Na1-Ow1	87.46(6)
Na1-O8′	2.339(2)	O5′-Na1-O5	86.33(6)	Ow2-Na1-Ow1	70.82(6)
Na1-Ow1	2.405(2)	O5′-Na1-O8′	89.63(6)	O8′-Na1-Ow1	83.20(6)
Na1-Ow2	2.563(2)	O8′-Na1-Ow2	87.59(6)	O5′-Na1-Ow1	78.26(6)
Mean	2.422				
Eightfold coordination around Na2 (distorted)					
Na2-O1′	2.683(2)	O8′-Na2-O7′	110.84(6)	O5′-Na2-O6″	55.63(5)
Na2-O2′	2.652(2)	O8′-Na2-O5′	88.73(6)	O6′-Na2-O6″	69.21(6)
Na2-O5′	2.468(2)	O8′-Na2-O6′	84.16(6)	O2′-Na2-O6″	74.92(5)
Na2-O6′	2.590(2)	O7′-Na2-O6′	56.69(5)	O8′-Na2-O1′	95.23(6)
Na2-O6″	2.652(2)	O5′-Na2-O6′	86.10(5)	O5′-Na2-O1′	76.40(5)
Na2-O7′	2.411(2)	O2′-Na2-O7′	88.99(5)	O2′-Na2-O1′	53.23(5)
Na2-O8′	2.405(2)	O2′-Na2-O5′	99.44(6)	O6″-Na2-O1′	100.17(5)
Na2-Ow4′	2.972(2)	O6″-Na2-O7′	83.98(5)	O2′-Na2-Ow4′	68.64(5)
Mean	2.604				
Tetrahedral coordination around S1 and S2					
S1-O5	1.472(2)	O5-S1-O6	109.33(9)	O8-S1-O5	109.91(9)
S1-O6	1.463(2)	O8-S1-O6	111.09(9)	O5-S1-O7	108.83(9)
S1-O7	1.492(2)	O7-S1-O6	107.24(9)	O8-S1-O7	110.38(9)
S1-O8	1.470(2)				
Mean	1.474				
S2-O1	1.473(2)	O3-S2-O1	110.25(9)	O3-S2-O4	110.01(9)
S2-O2	1.479(2)	O3-S2-O2	109.24(9)	O1-S2-O4	110.02(9)
S2-O3	1.471(2)	O1-S2-O2	108.13(9)	O2-S2-O4	109.15(9)
S2-O4	1.481(2)				
Mean	1.476				

bonding. The structure determination was confirmed using the bond-valence summation method (Brown 1981), the results of which are presented in Table 8.

Description of the structure

The unit-cell parameters refined for konyaite in this study are consistent with those reported by van Doesburg et al. (1982) (Table 2). The konyaite structure contains three cation sites. Magnesium is octahedrally coordinated by both oxygen and water molecules. Both Na polyhedra (six- and eight-coordinated) are significantly distorted, whereas the Mg octahedra are only slightly distorted. Each coordination polyhedron shares at least one edge with either a neighboring cation site or one of two symmetrically distinct sulfate tetrahedra. This arrangement creates infinite sheets perpendicular to *b*, accounting for the {010} tabular habit of konyaite, and its {010} cleavage. Hydrogen bonds provide the inter-sheet linkage.

Each sheet is composed of chains of eight-coordinated Na (Na2), Mg octahedra and sulfate tetrahedra running parallel to *a*. They are connected by two edge-sharing octahedral Na sites (Na1). The repeating unit that forms each chain consists of the two Na2 sites, sharing an edge between them, and three additional edges, one with the same S1 tetrahedron, a second with a S2

TABLE 7. Hydrogen bonds (d in Å) and angles (< in °) for konyaite

D-H···A	d(D-H)	d(H···A)	d(D···A)	< D-H-A	Water molecule	< H-Ow-H
Ow1-H1A···Ow3	0.79(3)	2.16(3)	2.931(2)	165(3)		
Ow1-H1B···O6	0.72(3)	1.98(3)	2.692(2)	173(3)		
Ow2-H2A···O4	0.81(3)	2.00(3)	2.771(2)	159(3)	H1A-Ow1-H1B	108(3)
Ow2-H2B···O1	0.84(3)	1.91(3)	2.747(2)	176(3)	H2A-Ow2-H2B	104(3)
Ow3-H3A···O2	0.77(3)	1.97(3)	2.713(2)	162(3)	H3A-Ow3-H3B	101(3)
Ow3-H3B···O3	0.86(3)	1.85(3)	2.716(2)	176(3)	H4A-Ow4-H4B	102(3)
Ow4-H4A···O3	0.85(3)	1.97(3)	2.781(2)	160(3)	H5A-Ow5-H5B	106(3)
Ow4-H4B···O2	0.82(3)	1.93(3)	2.746(2)	173(3)		
Ow5-H5A···O4	0.80(4)	1.94(3)	2.734(2)	177(4)		
Ow5-H5B···O4	0.79(4)	2.03(4)	2.777(2)	159(4)		

Note: D = donor; A = acceptor; d = distance.

tetrahedron, and a third with a Mg octahedron that consequently shares a corner with the central S1 tetrahedron (Fig. 2a). These repeating units are linked together through corner-sharing between the S1 tetrahedra of one unit and the Na2 sites of the next. Figure 2b illustrates the chain arrangement, and Figure 2c shows the Na1 linkage. Each Na1 octahedron shares two edges with the Mg octahedron and the eight-coordinated Na2 site of a particular chain, and an edge with another Na1 octahedron, effectively linking the chains together and forming sheets perpendicular to *b*. Consequently, each Na1 site also shares a corner with both S1 and S2 tetrahedra.

The five water molecules present in konyaite are primarily bonded to the Mg octahedron, but, due to the compact nature of the structure, they are also coordinated to both Na sites. Most hydrogen atoms are therefore located on the outside of each sheet, but only H3 and H5 atoms serve to link the sheets together, whereas the others participate exclusively in intra-sheet bonding (Fig. 2d). All hydrogen atoms bond chiefly to the O atoms of the sulfate group, and secondly to the O atoms of other water molecules.

Bond lengths and angles

The Mg octahedron of konyaite is slightly distorted, with Mg-O distances varying between 2.03 and 2.10 Å. The mean Mg-O bond length of 2.06 Å is reasonable when compared to the results obtained in similar structures (Hawthorne 1985), and agrees well with the sum of the ionic radii reported by Shannon (1976). Both Na polyhedra are also distorted, the eight-coordinated Na2 site more so than the octahedrally coordinated Na1 site. Interatomic distances for the Na1-O bonds have a mean value of 2.42 Å, compared to 2.37 Å for similar structures, and the Na2-O bonds are likewise longer, at 2.60 Å compared to 2.53 Å (Shannon 1976). The internal angles of both the octahedra and the Na-dodecahedra therefore differ significantly from their ideal values. Both sulfate tetrahedra display nearly ideal configurations.

Hydrogen bonds

Shannon (1976) reports an average value of 0.97 Å for the short O-H bond associated with water molecules. The calculated bond lengths reported in Table 7 are substantially shorter, averaging 0.81 Å. This discrepancy is a direct consequence of the chosen method of crystal analysis, as reported by Dai et al. (1995). X-ray diffraction relies on the measure of electron density to locate atoms, rather than on interactions with the nucleus. Closely associated atoms, such as the O-H pairs in the water molecule, tend to have poorly separated electron distributions. Measured interatomic distances are, consequently, systematically shorter than values obtained by other methods, such as neutron diffraction. For the purpose of the bond valence summation calculations presented in Table 8, the short hydrogen bonds of the refined structure were therefore defined as being 0.97 Å in length (Shannon 1976), to account for this systematic error. The long hydrogen bond distances were also determined to be approximate, and their contributions to bond valence were calculated from the curve presented by Ferraris and Ivaldi (1988). This curve allows for the calculation of the bond valence of an H···O bond based on its O···O distance, therefore eliminating the need to know the precise position of the hydrogen atom. The summation, with these corrections, supports the refined atomic structure. The hydrogen bonding arrangement described here was also compared with the curve from Ferraris and Franchini-Angela (1972). This curve suggests that the upper limit for the H···O distance of reasonable hydrogen bonds within crystalline substances is 2.5 Å, with an O-H···O angle greater than 130°. The hydrogen bonds presented in this study (Table 7) are well within those limits, keeping in mind that they are approximate.

Relationship to blödite

Konyaite is a common phase of saline soils (Keller et al. 1986a; Zielinski et al. 2001). High solution concentrations and rapid evaporation rates favor the precipitation of konyaite in

TABLE 8. Bond valences (v.u.) for konyaite

	O1	O2	O3	O4	O5	O6	O7	O8	Ow1	Ow2	Ow3	Ow4	Ow5	Sum	R_o/b/N
Mg							0.39		0.37	0.33	0.37	0.35	0.37	2.18	1.636 / 0.42 / –
Na1	0.18				0.15 ×2 →↓			0.21	0.19	0.13				1.01	1.661 / 0.44 / –
Na2	0.10	0.11			0.16	0.12 ×2 →↓	0.18	0.18				0.05		1.02	1.661 / 0.44 / –
S1					1.48	1.52	1.40	1.49						5.89	1.614 / 0.36 / –
S2	1.48	1.46	1.49	1.45										5.88	1.614 / 0.36 / –
H1A									0.79		0.15			0.94	0.87 / – / 2.2
H1B						0.23			0.79					1.02	0.87 / – / 2.2
H2A				0.19						0.79				0.98	0.87 / – / 2.2
H2B	0.20									0.79				0.99	0.87 / – / 2.2
H3A		0.22									0.79			1.01	0.87 / – / 2.2
H3B			0.22								0.79			1.01	0.87 / – / 2.2
H4A			0.19									0.79		0.98	0.87 / – / 2.2
H4B		0.21										0.79		1.00	0.87 / – / 2.2
H5A				0.21									0.79	1.00	0.87 / – / 2.2
H5B				0.19									0.79	0.98	0.87 / – / 2.2
Sum	1.96	2.00	1.90	2.04	1.94	1.99	1.97	1.88	2.14	2.04	2.10	1.98	1.95		

Note: Multiplicity is indicated by × →↓, constants were obtained from Brown (1981), long hydrogen bond valences were determined from the $s_{(H\cdots O)}$ vs. O···O curve of Ferraris and Ivaldi (1988), where $s = [(O\cdots O)/2.17]^{-8.2} + 0.06$.

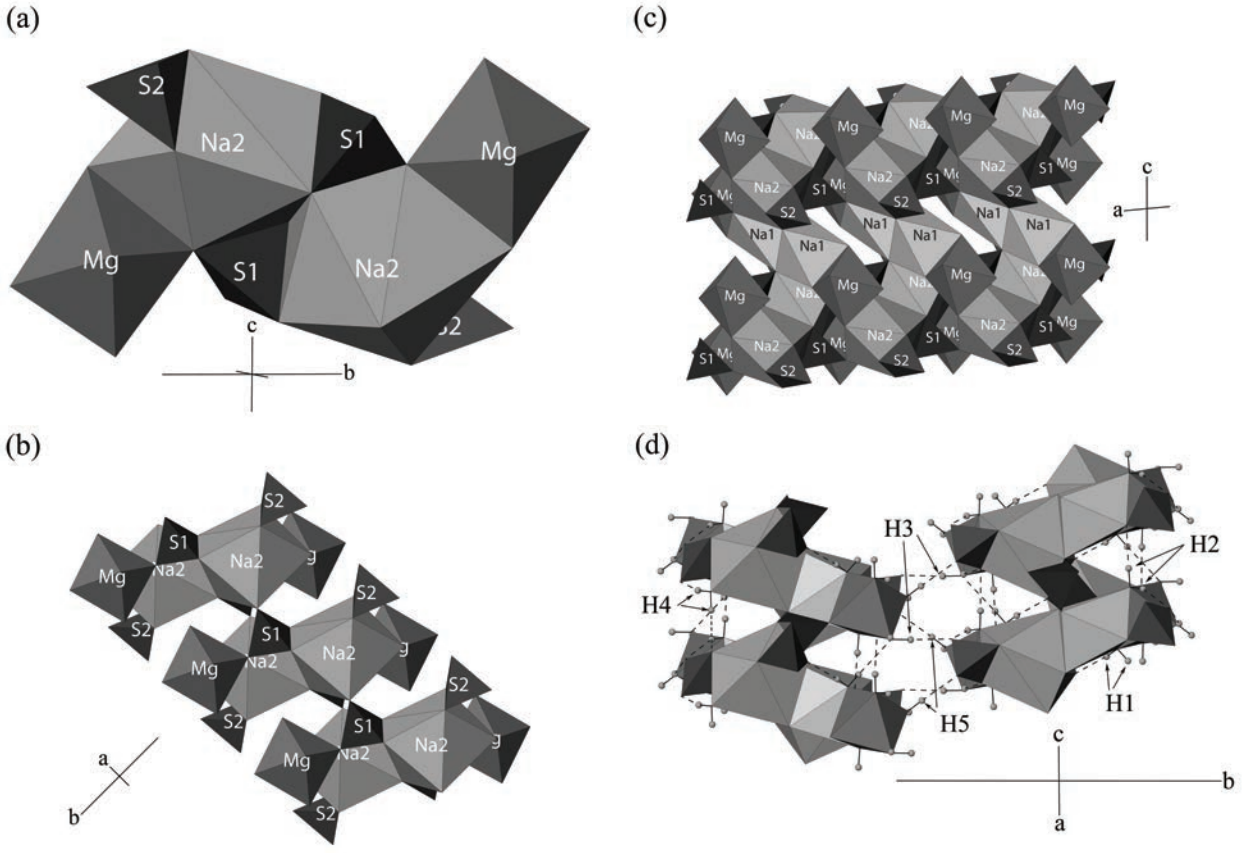

FIGURE 2. The structure of konyaite, $Na_2Mg(SO_4)_2 \cdot 5H_2O$, created from the crystallographic data and atomic coordinates refined in this study and the Shape Software program ATOMS, v.6.0 (Dowty 2003). (**a**) Fundamental repeating unit of the structure, as viewed approximately down the *a* axis and perpendicular to *c*. The O atoms of the five water molecules coordinate the Mg octahedra. (**b**) Polymerization of the fundamental repeating unit, as viewed down the *c* axis and perpendicular to *a*. The units are connected to one another through corner-sharing of the S1 tetrahedra and the Na2 polyhedra. (**c**) Single sheet of the konyaite structure, as viewed down the *b* axis, and perpendicular to the *a*-*c* plane. The paired Na1 octahedra serve to link one set of polymerized units to another, through edge-sharing with the Mg and Na2 polyhedra of each set. (**d**) The konyaite structure as viewed at β/2 from the *c* axis and perpendicular to the *b* axis. Small gray spheres represent hydrogen atoms. Sheets are linked together through hydrogen bonding exclusively. H3 and H5 atoms only participate in inter-sheet linkage, while H1, H2, and H4 atoms only form intra-sheet bonds. This geometry accounts for the {010} tabular habit of konyaite and its perfect {010} cleavage.

the Na_2O-MgO-SO_4-H_2O system (Shayan and Lancucki 1984). The mineral appears to form in disequilibrium with its parent saline solution, and to alter to blödite within a matter of days at room temperature, if the crystals stay in contact with the solution (Friedel 1976). This lifespan can be extended if the RH is increased, but it is still limited. However, if removed from its parent solution, konyaite has been shown to persist for up to 90 days, even well below 80% relative humidity (Timpson et al. 1986). The conversion of konyaite to blödite is not dictated only by temperature and humidity: crystal size is reported to be an important factor (van Doesburg et al. 1982). Larger crystals take longer to dehydrate to blödite, implying that diffusion rates and reaction kinetics are an important factor in the dehydration of konyaite (Timpson et al. 1986). A well-defined stability field for konyaite has yet to be determined. It was originally believed that konyaite would only form at temperatures between 30 and 50 °C (van Doesburg et al. 1982), but Keller et al. (1986a) have since reported the presence of konyaite between 6.3 and 37.9 °C. However, certain stability relationships have been mapped out: it is possible to synthesize konyaite between 24 and 28 °C and 51 and 79% RH (this study), and Keller et al. (1986b) has obtained konyaite at 28 and 40 °C and 20% RH as well, pointing out that the range of solution compositions from which konyaite can precipitate shrinks at lower temperatures. Further investigations of the Na_2O-MgO-SO_4-H_2O system are underway and phase relationships will be carefully studied. In situ powder X-ray diffraction experiments of natural samples may provide valuable insight into the hydration-dehydration reactions involving blödite, konyaite, and other related hydrate phases.

From a structural point of view, both blödite and konyaite are monoclinic and have sheet structures. However, konyaite has a much more densely packed sheet arrangement than blödite's open sheet configuration (Hawthorne 1985), where polyhedra share mostly corners, and only the two Na polyhedra share edges. In contrast, all the polyhedra in the konyaite structure share edges (up to three) with neighbors, and no polyhedra are bonded only

by vertices.

The sheets of the blödite structure (Fig. 3a) are composed of $[^{VI}M(^{IV}T\Phi_4)_2\Phi_4]$[2] clusters, where water-coordinated Mg octahedra share corners with two sulfate tetrahedra (Hawthorne 1985). These clusters are linked by pairs of a symmetrically unique Na octahedral site, and by hydrogen bonds to form open sheets. These sheets are in turn bonded to one another through corner-sharing between the sulfate tetrahedra and Mg and Na octahedra, and further hydrogen bonding (Fig. 3b).

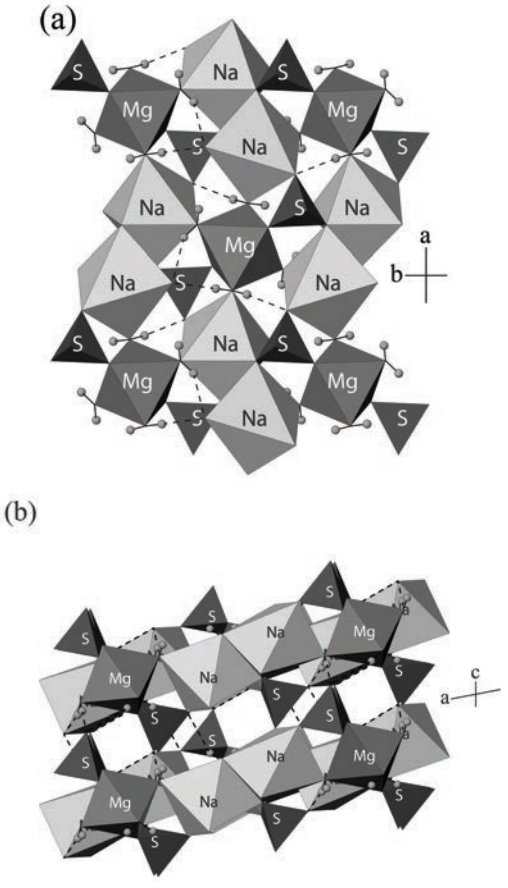

FIGURE 3. The structure of blödite, $Na_2Mg(SO_4)_2\cdot 4H_2O$, created from the crystallographic data and atomic coordinates of Hawthorne (1985) and the Shape Software program ATOMS, v.6.0 (Dowty 2003). (**a**) Open sheet, as seen down the *c* axis. The four water molecules coordinate the magnesium octahedra through their oxygen atoms. Small gray spheres represent hydrogen atoms. The sheets of $[^{VI}M(^{IV}T\Phi_4)_2\Phi_4]$ clusters (Mg octahedra and their two associated sulfate tetrahedra) are held together by hydrogen bonds and the paired Na octahedra. (**b**) Inter-sheet linkage, as seen down the *b* axis and perpendicular to the *a*-*c* plane. The open sheets are linked to one another both through hydrogen bonding and corner sharing between the S1 tetrahedra of one sheet and the Na octahedra of another.

[2] $[^{VI}M(^{IV}T\Phi_4)_2\Phi_4]$ refers to a cluster having a six-coordinated transition metal site (in this case, $^{VI}M = Mg^{2+}$), bonding with two sulfate groups $(^{IV}T\Phi_4)_2$ and four water molecules ($\Phi_4 = 4H_2O$). In this case, $^{IV}T = S^{+6}$ and is in tetrahedral coordination with four O atoms, $\Phi_4 = O^{2-}$.

The konyaite structure, on the other hand, is composed of a significantly different Mg-SO_4 arrangement. Each Mg octahedron shares only one corner with one sulfate tetrahedron. The second sulfate tetrahedron is linked to the Mg octahedron only through hydrogen bonding, but shares an edge and a corner with each of the Na sites. The presence of five water molecules in konyaite, as opposed to the four in blödite, leads to two distinct Na sites. Both sites occur in edge-sharing pairs, much like those in blödite, with the exception that the eight-coordinated site serves as the core of infinite Mg-SO_4 chains, while the pairs of octahedra link the chains together to form the sheets. Such a chain-like arrangement is not found in blödite. In addition, the konyaite structure relies solely on hydrogen bonding between sheets, whereas in blödite the sulfate tetrahedra are also involved in bonding between sheets. The details of the reaction mechanisms have yet to be described, but it is clear that the dehydration of konyaite to blödite involves more than the simple loss of one water molecule. Significant changes in the linkage of all the polyhedra and a reorganization of the Na coordination to eliminate the difference between the two distinct Na sites are necessary.

ACKNOWLEDGMENTS

We would like to thank G. Ferraris and M. Welch, as well as an anonymous reviewer for their very helpful comments on the manuscript, and I. Swainson for editorial assistance. We also gratefully acknowledge the support of the Natural Sciences and Engineering Research Council of Canada in the form of a Discovery grant to R.C.P. and a Postgraduate Scholarship to E.M.S.L.

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Manuscript received October 29, 2008
Manuscript accepted February 24, 2009
Manuscript handled by Ian Swainson