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THE CRYSTAL STRUCTURE OF HUMBERSTONITE, A MIXED SULFATE–NITRATE MINERAL

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ABSTRACT

The crystal structure of humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2{\cdot}6H_2O$, rhombohedral, *a* 10.9055(3), *c* 24.3949(9) Å, *V* 2512.6(2) Å^3, space group $R\bar{3}$, $Z = 3$, has been refined using the Rietveld method and transmission powder X-ray diffraction data collected with monochromated $CuK\alpha_1$ radiation. Final $R_{BRAGG} = 9.1\%$, $R_{WP} = 18.0\%$, GOF = 2.27. Humberstonite is isostructural with ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2{\cdot}6H_2O$. In ungemachite, there are two Na positions, Na(1) and Na(2), which are completely occupied by Na, and are both [6]-coordinated, and one Fe^{3+} position that also is [6]-coordinated. In humberstonite, Na(2) is completely occupied by Na, and Mg occupies the position analogous to Fe^{3+} in ungemachite; however, the Na(1) position in humberstonite is occupied by both Na and Mg in equal proportions. The 50:50 Na–Mg occupancy of Na(1) is a consequence of electroneutrality requirements, and we did not observe signs of Na–Mg ordering (*i.e.*, no supercell reflections were observed).

Keywords: humberstonite, nitrate, sulfate, Rietveld, structure refinement.

SOMMAIRE

La structure cristalline de la humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2{\cdot}6H_2O$, minéral rhomboédrique, *a* 10.9055(3), *c* 24.3949(9) Å, *V* 2512.6(2) Å^3, groupe spatial $R\bar{3}$, $Z = 3$, a été affinée par moindres carrés en utilisant la méthode de Rietveld et des données de diffraction X obtenues sur poudres par transmission avec rayonnement monochromatique $CuK\alpha_1$. L'indice R_{BRAGG} est égal à 9.1%, l'indice R_{WP}, à 18.0%, et l'indice de concordance interne des données, à 2.27. La humbersonite possède la même structure que la ungemachite, $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2{\cdot}6H_2O$. Dans cette dernière, le sodium occupe deux positions distinctes, Na(1) et Na(2), à coordinence [6], et le Fe^{3+} occupe une position, aussi à coordinence [6]. Dans la humberstonite, le sodium occupe la position Na(2), tandis que le Mg occupe la position du Fe^{3+} de la ungemachite. Na et Mg occupent la position Na(1) en proportions égales dans la humberstonite. Cette présence de Na et Mg en proportions égales est une conséquence des exigeances d'électroneutralité; nous n'avons décelé aucun signe de mise en ordre impliquant Na et Mg, et donc aucun indice d'une surstructure.

(Traduit par la Rédaction)

Mots-clés: humbersonite, nitrate, sulfate, Rietveld, affinement de la structure.

INTRODUCTION

Humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2{\cdot}6H_2O$, found in the nitrate fields in the Atacama Desert, was described by Mrose *et al.* (1970). There, it occurs in layers up to 40 cm thick, associated with bloedite and nitratine. Mrose *et al.* (1970) derived the unit cell and space group for humberstonite and noted that the crystallographic data are similar to those of ungemachite, which had been erroneously defined as $K_3Na_8Fe^{3+}(SO_4)_6(OH)_2{\cdot}10H_2O$ by Peacock & Bandy (1938). However, the different chemical formulae of these two minerals led Mrose *et al.* (1970) to suggest that they are not isostructural, although the structures were assumed to be closely related. The structure determination for ungemachite (Groat & Hawthorne 1986) revealed the presence of a nitrate group, and gave the revised formula $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2{\cdot}6H_2O$. This revised formula led us to suspect that humberstonite and ungemachite are isostructural.

We obtained several grams of humberstonite from the Atacama Desert, Chile, and planned to refine the structure. However, we were unable to find a crystal large enough for single-crystal study; the crystals are hexagonal plates with maximum diameters of ~ 0.1 mm but only ~ 0.01 mm thick, resulting in very low crystal volumes and poor intensities of diffraction maxima. Fortunately, we had sufficient sample to proceed with a Rietveld structure-refinement from X-ray powder data, which not only shows that humberstonite is isostructural with ungemachite, but also provides refined positional coordinates for the former.

EXPERIMENTAL

Samples were prepared for transmission-geometry X-ray powder diffraction experiments by spreading small amounts of ground humberstonite onto a 4-μm-thick XRF Prolene film using hairspray as a mounting medium. In transmission geometry, the X-ray beam must pass through the sample, and sample thickness is critical. Thin samples give poor peak/background ratios, whereas thick samples absorb all of the radiation. Several samples of various thickness were prepared: the sample (≈ 25 mg) that gave the highest peak/background ratio was used for data collection.

Data were collected using a Siemens D5000 automated X-ray powder-diffractometer operating in transmission geometry. A Huebner incident-beam monochromator was used to obtain Cu$K\alpha_1$ X-radiation generated using 40 kV and 35 mA with a fine-focus X-ray tube. The sample, positioned perpendicular to the incident beam at $\theta = 0$, was rotated at 120 rpm during the $\theta/2\theta$ scan. A 2-mm antiscatter slit, a 0.1-mm receiving slit, and a Kevex solid-state detector were used. Data were collected over the angular range $8 \leq 2\theta \leq 105°$ using a step width of 0.02°, with 15 s spent counting at each step. Peak widths (FWHM) at low angles were approximately equal to 0.10°2θ.

STRUCTURE REFINEMENT

The Rietveld structure-refinement was done using the program DBWS–9006PC (Sakthivel & Young 1990) installed on an IBM RS–6000 computer. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography (1974). *R*-indices are of the form given in Table 1, and expressed as percentages.

TABLE 1. MISCELLANEOUS INFORMATION FOR HUMBERSTONITE

a (Å)	10.9055(3)	R_{BRAGG}	9.1 %
c (Å)	24.3949(9)	R_P	14.3 %
V (Å^3)	2512.6(2)	R_{WP}	18.0 %
		D-W*	0.73
Space group	R$\bar{3}$	GOF** 2.27	
Data range	($8 \leq 2\ \theta \leq 105°$)	Step width	0.02°
Radiation	Cu$K\alpha_1$	Count/step	15 s

Unit-cell contents: $3[K_3Na_7Mg_2(SO_4)_6(NO_3)_2{\cdot}6H_2O]$

$R_{BRAGG} = 100\Sigma|I_o\text{-}I_c|/\Sigma I_o$

$R_P = 100\Sigma|y_i\text{-}y_{ci}|/\Sigma|y_i|$, y_i = intensity at step i

$R_{WP} = 100\{\Sigma w_i(y_i\text{-}y_{ci})^2/\Sigma w_i y_i^2\}^{½}$

* D-W = Durbin-Watson D-statistic
** GOF = Goodness-of-fit = $[R_{WP}/R_{exp}]^2$

TABLE 2. ATOMIC PARAMETERS FOR HUMBERSTONITE

Site		x	y	z	B*
N	6c	1/3	2/3	0.0926(9)	2.1(9)
S	18f	0.3437(7)	0.171(2)	0.2747(2)	1.0(1)
K	9e	1/2	0	0	0.9(2)
Mg	3a	0	0	0	0.3(5)
Na(1)$^+$	6c	0	0	0.1250(6)	1.6(3)
Na(2)	18f	0.6459(7)	0.821(2)	0.0917(3)	0.9(2)
O(1)	18f	0.501(1)	0.257(3)	0.2754(5)	0.9(1)
O(2)	18f	0.285(1)	0.128(2)	0.3274(5)	0.9(1)
O(3)	18f	0.287(3)	0.248(2)	0.246(1)	0.9(1)
O(4)	18f	0.308(3)	0.033(3)	0.242(1)	0.9(1)
O(5)	18f	0.093(3)	0.895(3)	0.1693(5)	0.9(1)
O(6)	18f	0.417(2)	0.797(1)	0.0958(5)	0.9(1)

* Oxygen Bs were constrained to be identical
+ occupied by 50% Mg and 50% Na

The refinement was carried out in the space group $R\bar{3}$ (Mrose *et al.* 1970) over the range $8 \leq 2\theta \leq 105°$ using the atomic coordinates of ungemachite (Groat & Hawthorne 1986) as the starting model. The cations contained in the humberstonite formula were distributed over the available sites of the model structure, and site-scattering refinement was used to verify the assignments. Diffraction peaks were modeled using the Thompson – Cox – Hastings modified pseudo-Voigt profile-function corrected for asymmetry up to 30° 2θ. The background was modeled using a refined fifth-order polynomial. Humberstonite occurs as hexagonal plates parallel to (001), resulting in significant preferred orientation in prepared samples. The preferred orientation was taken into account in the Rietveld refinement using the Rietveld–Toraya function included in the program DBWS–9006PC. Initially, individual isotropic displacement parameters were fixed, and an overall displacement parameter was refined. This procedure tends to act as a combined absorption and extinction correction. In later cycles of refinement, individual isotropic displacement parameters were allowed to vary. The refinement converged to $R_{BRAGG} = 9.1\%$, $R_P = 14.3\%$ and $R_{WP} = 18.0\%$. Final unit-cell dimensions and miscellaneous information are given in Table 1, refined atomic parameters in Table 2, bond lengths, angles and polyhedral edge-lengths in Table 3, and a bond-valence analysis is given in Table 4. The observed profile is compared to the profile calculated using the refined structure-parameters in Figure 1.

DISCUSSION

Inspection of the observed and calculated profiles (Fig. 1) for humberstonite shows that the material used is pure and that all peaks are accounted for, indicating

TABLE 3. SELECTED INTERATOMIC-DISTANCES (Å) AND ANGLES (°) IN HUMBERSTONITE

N-O(6)	1.25(1) x3	Mg(1)-O(1)b	2.11(1) x6
S-O(1)	1.49(1)	Na(1)-O(1)b	2.26(1) x3
S-O(2)	1.41(1)	Na(1)-O(5)	2.16(1) x3
S-O(3)	1.44(3)	<Na(1)-O>	2.21
S-O(4)	1.57(3)		
<S-O>	1.49	Na(2)-O(2)g	2.40(1)
		Na(2)-O(3)h	2.58(4)
K-O(2)a,b	3.10(2) x2	Na(2)-O(4)i	2.36(4)
K-O(2)c,d	2.80(2) x2	Na(2)-O(5)j	2.40(1)
K-O(3)a,b	2.88(2) x2	Na(2)-O(6)	2.38(3)
K-O(4)c,d	2.96(2) x2	Na(2)-O(6)k	2.76(3)
K-O(6)e,f	3.03(1) x2	<Na(2)-O>	2.50
<K-O>	2.95		
NO_3 triangle			
O(6)-O(6)k	2.16(2) x3	O(6)-N-O(6)k	119.9(4) x3
SO_4 tetrahedron			
O(1)-O(2)	2.41(2)	O(1)-S-O(2)	112.8(8)
O(1)-O(3)	2.39(3)	O(1)-S-O(3)	109.5(1.8)
O(1)-O(4)	2.43(3)	O(1)-S-O(4)	105.2(1.8)
O(2)-O(3)	2.36(3)	O(2)-S-O(3)	112.3(1.6)
O(2)-O(4)	2.40(3)	O(2)-S-O(4)	107.1(1.6)
O(3)-O(4)	2.46(2)	O(3)-S-O(4)	109.6(8)
<O-O>	2.41	<O-S-O>	109.4
MgO_6 octahedron			
O(1)b-O(1)l	2.71(2) x6	O(1)b-Mg-O(1)l	80.1(5) x6
O(1)b-O(1)c	3.23(3) x6	O(1)b-Mg-O(1)c	99.9(5) x6
<O-O>	2.97	<O-Mg(1)-O>	90.0
$Na(1)O_6$ octahedron			
O(1)b-O(1)n	2.71(2) x3	O(1)b-Na(1)-O(1)n	73.6(6) x3
O(1)b-O(5)	3.22(3) x3	O(1)b-Na(1)-O(5)	93.3(9) x3
O(1)b-O(5)m	3.23(3) x3	O(1)b-Na(1)-O(5)m	93.7(1.0) x3
O(5)-O(5)m	3.25(2) x3	O(5)-Na(1)-O(5)m	97.2(6) x3
<O-O>	3.10	<O-Na(1)-O>	89.4
$Na(2)O_6$ trigonal prism			
O(2)g-O(3)h	2.36(3)	O(2)g-Na(2)-O(3)h	85.6(8)
O(2)g-O(4)i	2.40(3)	O(2)g-Na(2)-O(4)i	94.6(5)
O(2)g-O(6)	3.33(2)	O(2)g-Na(2)-O(6)	88.1(4)
O(2)g-O(6)k	3.50(2)	O(2)g-Na(2)-O(6)k	85.1(4)
O(3)h-O(5)j	2.59(4)	O(3)h-Na(2)-O(5)j	86.4(1.1)
O(3)h-O(6)k	3.37(3)	O(3)h-Na(2)-O(6)k	78.4(7)
O(4)i-O(5)j	2.71(4)	O(4)i-Na(2)-O(5)j	80.1(1.1)
O(4)i-O(6)	2.98(3)	O(4)i-Na(2)-O(6)	78.0(9)
O(5)j-O(6)	4.15(3)	O(5)j-Na(2)-O(6)	120.6(7)
O(5)j-O(6)k	4.54(3)	O(5)j-Na(2)-O(6)k	123.0(7)
O(6)-O(6)k	3.10(3)	O(6)-Na(2)-O(6)k	49.0(5)
<O-O>	3.18	<O-Na(2)-O>	88.1

a: ⅓+x, ⅔+y-1, ⅔+z-1; b: ⅔-x, ⅓-y, ⅓-z; c: ⅓-y, ⅔+x-y, ⅔+z-1; d: ⅔+y, ⅓-x+y, ⅓-z; e: x, y-1, z; f: 1-x, 1-y, 1-z; g: ⅓+x, ⅔+y, ⅔+z-1; h: ⅔+x-y, ⅓+x, ⅓-z; i: ⅔+y, ⅓-x+y, ⅓-z; j: y-x+1, -x, z; k: y-x, -x, z; l: ⅔+y-1, ⅓+y-x, ⅓-z; m: -y, x-y, z; n: ⅔+x-y-1, ⅓+x-1, ⅓-z.

the correct space-group. The refinement confirms that humberstonite is isostructural with ungemachite (Groat & Hawthorne 1986). The humberstonite structure is illustrated in Figure 2.

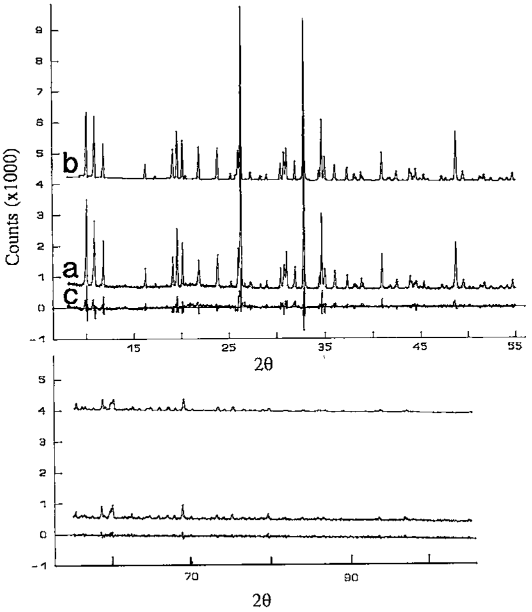

FIG. 1. Observed and calculated powder-patterns for humberstonite. (a) observed (+500 counts); (b) calculated using refined structure-parameters (+4000 counts); (c) residual (I_o–I_c).

Site populations

Comparison of the humberstonite and ungemachite formulae indicates that 1 Fe^{3+} and 1 Na per formula unit (pfu) in the ungemachite structure are replaced by 2 Mg pfu in the humberstonite structure. Two sites in the structure are octahedrally coordinated and may be occupied by Mg; these are the 3*a* position (occupied by Fe^{3+} in ungemachite) and the 6*c* position (occupied by Na in ungemachite). Site-scattering indicates that Mg occurs at the 3*c* site in humberstonite, and the <Mg–O> distance, 2.11 Å, is consistent with this assignment. However, this only accounts for 1 Mg pfu. Comparison of the formula of ungemachite and humberstonite suggests that Na and Mg are disordered over one site in humberstonite. There are two Na sites in this structure type: Na(1), which occupies a 6*c* position, and Na(2), which occupies an 18*f* position. Na ($Z = 11$) and Mg ($Z = 12$) scatter X rays in a very similar manner and cannot easily be distinguished by this means. However, they have very different ionic radii ($^{[6]}Mg = 0.72$, $^{[6]}Na = 1.08$ Å) and hence may be distinguished on the basis of mean bond-length. The mean bond-lengths at the Na(1) site in humberstonite and ungemachite are 2.21 Å (Table 3) and 2.41 Å, respectively, which may be compared with a value of 2.11 Å for <Mg–O> at the Mg site in humberstonite.

TABLE 4. BOND-VALENCE* (v.u.) ANALYSIS FOR HUMBERSTONITE

	S	N	K	Mg(1)	Na(1)	Na(2)	H(1)**	H(2)**	Σ
O(1)	1.44			$0.32\downarrow^{\times 6}$	$0.22\downarrow^{\times 3}$				1.98
O(2)	1.78		$0.07\downarrow^{\times 2}$ $0.13\downarrow^{\times 2}$			0.19			2.17
O(3)	1.64		$0.11\downarrow^{\times 2}$			0.13		(0.3)	2.18
O(4)	1.16		$0.10\downarrow^{\times 2}$			0.21	(0.3)		1.77
O(5)					$0.28\downarrow^{\times 3}$	0.19	(0.7)	(0.7)	1.87
O(6)		$1.72\downarrow^{\times 3}$	$0.08\downarrow^{\times 2}$			0.19 0.08			2.07
Σ	6.02	5.16	0.98	1.92	1.50	0.99	(1.0)	(1.0)	

* Parameters from Brown (1981)

** Assumed bond-valences

This indicates an Na(1) site-population of 50% Mg + 50% Na in humberstonite, and the bond-valence analysis (Table 4) supports this distribution of the cations.

The 50:50 substitution of Mg for Na is the result of electroneutrality requirements; the relation between the two species is given by the substitution 2 Mg $\rightleftharpoons$ Na + Fe^{3+}. The population of the Na(1) site suggests the possibility of subgroup or supercell ordering; we examined the low-angle regions of the powder-diffraction spectrum very carefully, but did not observe any supercell reflections.

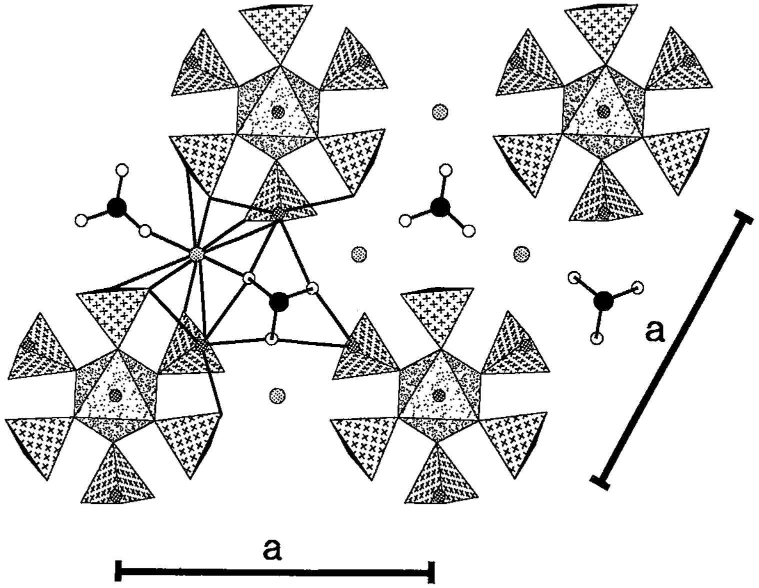

FIG. 2. The structure of humberstonite viewed down [001]. (MgO_6) octahedra are shaded with a random dot pattern, (SO_4) tetrahedra are shaded with crosses, Na atoms are cross-hatched circles, K atoms are dotted circles, N and O atoms are solid and open circles, respectively. N–O and selected Na–O and K–O bonds are given as solid lines.

TABLE 5. MINIMUM-ENERGY HYDROGEN POSITIONS IN HUMBERSTONITE

	x	y	z
H(1)	0.7653	-0.1845	0.1889
H(2)	0.7708	-0.0299	0.1889

O(5)-H(1)	0.99 Å	O(5)-H(1)-O(4)	161.2°
H(1)-O(4)	1.75		
O(5)-H(2)	0.96	O(5)-H(2)-O(3)	153.4
H(2)-O(3)	1.69		
H(1)-H(2)	1.62	H(1)-O(5)-H(2)	111.1

Hydrogen bonding

Hydrogen bonding in ungemachite links heteropolyhedral sheets that are parallel to (001); bond-valence requirements (Table 4) are consistent with the same hydrogen-bonding scheme in humberstonite. The O(5) oxygen is the central atom of an H_2O group, and O(3) and O(4) are the hydrogen-bond acceptors. Minimum-energy hydrogen-atom positions were calculated using the program WMIN (Busing 1981) and the hydrogen positions in ungemachite (Groat & Hawthorne 1986) as starting values. The H–O and H...O interactions were modeled using the directionally isotropic potential of Abbott *et al.* (1989), as applied in the study of hydrogen bonding in borate minerals by Burns & Hawthorne (1993a,b). The Born short-range repulsion energy parameters ρ_{ij} = 0.25 Å and λ_{ij} = 26500 kJ/mole were used. The calculated hydrogen-positions and the hydrogen-bonding scheme (Table 5) agree with those experimentally observed in ungemachite (Groat & Hawthorne 1986).

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