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The crystal structure of lüneburgite, $Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]$

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ABSTRACT

Lüneburgite, $Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]$, is triclinic, $P\bar{1}$, with $a = 6.3475(6)$, $b = 9.8027(11)$, $c = 6.2976(5)$ Å, $\alpha = 84.46(1)$, $\beta = 106.40(1)$, $\gamma = 96.40(1)°$, and $Z = 1$. Its structure has been refined to an unweighted residual of 0.026 using 2069 reflections. The structure consists of T_2M-M-T_2M sandwiches stacked along **b*** with adjacent sandwiches only connected by H bonds. The fundamental cluster in the T_2M layers is a Mg(2) octahedron connected to a B-P tetrahedral pair. All the tetrahedra in a T_2M layer have their apices pointing in the same direction. The apices of the tetrahedra in the upper T_2M layer in a T_2M-M-T_2M unit point down into the interior of the unit, and the apices of the tetrahedra of the lower T_2M layer point up into the interior of the unit. The upper and lower T_2M layers are bridged by Mg(1) octahedra. Extensive H bonding exists within T_2M-M-T_2M units as well as between them. Two small intersecting channels run parallel to **a** and **c** within each T_2M-M-T_2M unit. The diameter of each channel, excluding H bonds, is approximately 4 Å.

INTRODUCTION

Lüneburgite is a triclinic hydrated basic borate-phosphate of Mg, and the solution of its crystal structure has eluded investigators for many years. It is mainly found in sediments and sedimentary rocks in or associated with marine evaporite sequences. The type material from marl at Lüneburg, Germany, was first described by Noellner in 1870. Lüneburgite has since been found at a number of other localities (see a partial review in Kuehn, 1972; Godlevsky and Ivanov, 1941; Kurman, 1958; Osinskii, 1960; Vakhrameeva and Voronova, 1960; Müller and Fabricius, 1978). At a majority of the localities lüneburgite occurs as spherules, nodules, streaks or flakes of millimeter size, and only rarely as small tabular to blocky crystals. Obradović et al. (1984) reported the occurrence of crystals up to 3 mm in maximum dimension from a sedimentary magnesite deposit at Bela Stena, Serbia, Yugoslavia. It is this material on which the present crystal structural investigation focuses.

The first single crystal X-ray data, reported by Braitsch (1961), suggested lüneburgite to be monoclinic with space group *A*2 or *Am*. A number of investigators in recent years have been stymied in their attempts at crystal structure work on lüneburgite by a lack of untwinned material.

OCCURRENCE AND CHARACTERIZATION

The lüneburgite occurs in a sedimentary magnesite deposit at Bela Stena, Serbia, Yugoslavia, as 0.5- to 3-mm crystals in magnesite, in association with dolomite and gypsum, and in voids in magnesite. In places, carbonate minerals are pseudomorphous after lüneburgite. The silicoborate howlite also occurs in the Bela Stena deposits (Stojanovic, 1967).

The translucent lüneburgite crystals are colorless and have a vitreous luster. They have a Mohs hardness of 2.0 and a measured specific gravity of 2.05. The material exhibits a fair {010} cleavage. Optically, the crystals are biaxial negative with $2V = 63°$. Refractive indices for Na light are $\alpha = 1.522(2)$, $\beta = 1.541(2)$, and $\gamma = 1.549(2)$. These results agree well with those of previous investigations.

CHEMICAL COMPOSITION

The unusually large size of the Bela Stena crystals made it possible to prepare concentrates of very high purity. Obradović et al. (1984) reported a wet chemical analysis of this material. Their results are given in Table 1 along with analyses of lüneburgite samples from other localities. The composition of the Bela Stena material corresponds most closely with that of lüneburgite from Lüneburg. The chemical analysis of the Bela Stena material yields a formula of $Mg_{3.2}(H_2O)_{6.1}[B_{1.8}(OH)_{5.5}(PO_4)_{2.1}]$.

A simultaneous DTA-TGA analysis of lüneburgite was carried out to aid in the characterization of the H_2O and OH. At 110 °C an endothermic event was recorded with a corresponding weight loss of 2.63%. This probably re-

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TABLE 1. Chemical analyses of lüneburgite

Oxides	Sample 1	2	3	4	5	6	7	8
P_2O_5	27.77	27.70	29.80	29.61	27.16	25.64	29.96	28.27
SiO_2		1.35				0.10		
B_2O_3	13.24	12.75	12.70	12.90	13.70	13.08	12.63	14.07
Fe_2O_3		0.63						
R_2O_3	0.60					0.20		
MgO	23.64	24.33	25.30	25.13	25.20	23.53	25.47	24.44
CaO		tr		0.15	0.10	tr	0.25	
Na_2O						0.33		
K_2O						0.36		
SO_3						0.57		
CO_2		1.64						
Cl						2.36		
H_2O^+	33.80	30.91	32.20	32.16	n.d.	27.21	31.61	32.78
H_2O^-						7.45		
n.d.	1.33							
Total	100.38	99.31	100.00	99.95		100.23	99.92	100.00

Note: Samples: 1 = Kerch Peninsula (Osinskii, 1960), 2 = Kerch Peninsula (Kurman, 1958), 3 = Lüneburg (Noellner, 1870), 4 = Lüneburg (Biltz and Marcus, 1912), 5 = E. Mediterranean Sea (Müller and Fabricius, 1978), 6 = Stebnik (Godlevsky and Ivanov, 1941), 7 = Bela Stena (Obradović et al., 1984), 8 = $Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]$.

flects the loss of nonessential H_2O (H_2O^-) from the surfaces of grains, cleavages, fractures and other crystal defect regions, and perhaps from channels. Four endothermic effects between 200 and 590 °C indicate loss of structural H_2O and OH totaling 27.28% by weight. An exothermic peak at 720 °C corresponds to destruction of the crystal structure. These results are very similar to those obtained by other investigators on lüneburgite from other localities (Ivanova, 1961).

EXPERIMENTAL METHOD

X-ray data on a single crystal of lüneburgite from Bela Stena, Yugoslavia, were measured using an automated Enraf-Nonius CAD-4 diffractometer and graphite monochromatized Mo$K\alpha$ radiation. Unit-cell parameters were obtained by least-squares refinement of the diffraction angles of 34 reflections in the 2θ range of 24 to 36°. The values determined are: $a = 6.3475(6)$, $b = 9.8027(11)$, $c = 6.2976(5)$ Å, $\alpha = 84.456(9)$, $\beta = 106.402(8)$, and $\gamma = 96.400(9)$°.

The intensity data were measured using the θ-2θ scan mode. The 2θ scan width was adjusted for dispersion by the equation $\theta = (A + B \tan \theta)$, where A = 1.0 and B = 0.34. Each reflection was scanned for a maximum of 60 s. Two-thirds of this time was spent on scanning the peak and one-third on determining the background. Three standard peaks were measured every 200 reflections, and no significant change in their intensities was observed during data collection.

A total of 2069 independent reflections was measured in the 2θ range 0.5–59.9°. The intensities were corrected for Lorentz, polarization, and absorption factors (the latter using ψ-scans). Experimental details are summarized in Table 2. The scattering factors for Mg, P, B, and O atoms were taken from the *International Tables for X-ray Crystallography* (1974). All calculations were carried out with the NRCVAX crystal structure programs (Gabe et al., 1989) on a Digital 8820 computer. The observed and calculated structure factors are given in Table 3.[1]

STRUCTURE DETERMINATION

Initial study centered on a crystal of lüneburgite from Mejillones, Chile, and its structure was solved using the SHELXS-86 program of Robinson and Sheldrick (1988). Least-squares refinement in space group *P*1 gave an *R* factor of 21%. Examination of the data suggested that the crystal was twinned on {110}. L. W. Finger kindly consented to apply his RFINE4 least-squares program (Finger and Prince, 1975) for twinned crystals to improve the refinement. It was found that roughly 30% of the volume of the crystal was indeed twinned relative to the remaining portion, and the twinning involved a 180° rotation about $[1\bar{1}0]$. With the twin correction, the isotropic and anisotropic *R* factors reduced to 10 and 7%, respectively, for refinement in space group $P\bar{1}$, with some of the atoms continuing to show nonpositive definite thermal ellipsoids.

About this time, some fine lüneburgite crystals from Bela Stena, Yugoslavia, became available. A colorless, prismatic, untwinned, euhedral crystal of dimensions 0.26 × 0.39 × 0.72 mm was used to measure new data. Using the atom positions previously determined from the twinned crystal, the new data were refined. The H positions were approximately located from difference Fourier maps. Attempts were made to refine the H positions by (1) refining *x*, *y*, *z*, and U_{ij} of the non-H atoms and *x*, *y*, *z*, and isotropic thermal parameters of H; (2) refining *x*, *y*, *z*, and *U* parameters of H alone first using all data and then using data up to $\sin \theta/\lambda = 0.48$; (3) refining only *x*,

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[1] A copy of Table 3 may be ordered as Document AM-91-460 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 2. Crystal and experimental data of lüneburgite

(A) Crystal-cell data		
a (Å)	6.3475(6)	α 84.46(1)
b (Å)	9.8027(11)	β 106.40(1)
c (Å)	6.2976(5)	γ 96.40(1)
V (Å^3)	372.69(6)	
FW	494.61	
F(000)	253.94	
Space group	$P\bar{1}$	
Z	1	
Formula	$Mg_3(H_2O)_6[B_2(OH)_6(PO_4)_2]$	
D_{calc} (g cm^{-3})	2.204	
D_{obs}	2.05	
μ (mm^{-1})	0.52	
(B) Intensity measurements		
Crystal size	0.26 × 0.39 × 0.72 mm	
Diffractometer	Enraf-Nonius Cad4	
Monochrometer	Graphite	
Radiation	Mo$K\alpha_1$(cell) (= 0.70926 Å) Mo$K\alpha$(data) (= 0.71069 Å)	
Scan type	θ–2θ	
2θ range	0.5–59.9	
Maximum counting time (s)	60	
The *h,k,l* ranges are	−8 8, 0 13, −8 8	
No. of reflections measured	2069	
No. of unique reflections	2069	
No. of reflections with $F_o > 3.0\sigma(F_o)$	2069	
Transmission factor range	0.4695, 0.6215	
(C) Refinement of the structure		
For significant reflections	*RF* 0.026, *Rw* 0.053.	
For all reflections	*RF* 0.026, *Rw* 0.053.	
"Goodness of fit" (GoF)	2.44	
where $RF = \mathrm{Sum}(F_o - F_c)/\mathrm{Sum}(F_o)$, $Rw = \mathrm{Sqrt}\{\mathrm{Sum}[w(F_o - F_c)^2]/\mathrm{Sum}(wF_o^2)\}$, and $\mathrm{Go}F = \mathrm{Sqrt}\{\mathrm{Sum}[w(F_o - F_c)^2]/(\text{no. of reflns.} - \text{no. of params.})\}$.		
Weights based on counting statistics	$w = \sigma^{2-}(F)$.	
Variable parameters	125.	
Maximum shift/sigma ratio	0.001.	
In the last difference synthesis, the largest minimum was −0.480e/Å^3 and the highest peak, 0.560e/Å^3.		
Secondary ext. coeff. = 0.993267	σ = 0.076053.	

TABLE 4a. Lüneburgite: atomic positional and isotropic thermal parameters

	x	*y*	*z*	B_{iso} (Å^2)
Mg(1)	0	0	0	0.821(22)
Mg(2)	0.33887(6)	0.66623(4)	−0.31919(6)	0.679(18)
P	0.24078(5)	0.72309(3)	0.13711(4)	0.570(16)
B	−0.12248(21)	0.71136(13)	−0.22907(20)	0.60(4)
O(1)	0.22712(15)	0.87371(9)	0.17200(15)	0.96(3)
O(2)	0.41127(15)	0.71210(9)	0.01082(14)	0.96(3)
O(3)	0.28952(15)	0.63511(9)	0.35400(14)	0.85(3)
O(4)	0.00992(14)	0.66280(9)	−0.00409(13)	0.82(3)
O(5)	−0.15042(15)	0.85815(9)	−0.22787(16)	1.04(3)
O(6)	0.00028(15)	0.69116(10)	−0.38998(15)	1.04(3)
O(7)	−0.33537(14)	0.63179(9)	−0.27715(15)	0.83(3)
O(8)	−0.21919(17)	0.91168(11)	0.20918(17)	1.48(4)
O(9)	0.39704(16)	0.87847(9)	−0.39107(15)	1.04(4)
O(10)	0.26772(15)	0.45615(10)	−0.24132(15)	1.02(3)
H(1)	0.2779	0.1276	0.2859	3.16
H(2)	0.0780	0.3599	0.4879	3.16
H(3)	0.3240	0.4464	0.3051	3.16
H(4)	0.6657	0.8588	0.1447	3.16
H(5)	0.8506	0.8667	0.3066	3.16
H(6)	0.6524	0.0656	0.3362	3.16
H(7)	0.3435	0.8946	0.4792	3.16
H(8)	0.8233	0.5581	0.1717	3.16
H(9)	0.6279	0.5878	0.1793	3.16

Note: B_{iso} of the non-H atoms is the mean of the principal axes of the thermal ellipsoid. For H B_{iso} is the isotropic Debye-Waller thermal parameter. Standard deviations in parentheses.

y, and *z* of H alone using data up to $\sin\theta/\lambda = 0.48$. In all cases, five of the bond distances involving structural H_2O were in the 0.68–0.77 Å range. In the final refinement, the positions of the H atoms obtained from the difference Fourier map were included but not refined. An isotropic thermal parameter, $U = 0.04$, was assigned to each H atom, and these parameters were not refined either. The final refined atomic and isotropic thermal parameters are listed in Table 4a and the non-H atom anisotropic thermal parameters in Table 4b. The final refinement converged to an *R* factor of 0.026 for all reflections (Table 2).

THE STRUCTURE OF LÜNEBURGITE

The structure of lüneburgite consists of Mg octahedra and B and P tetrahedra. The B and P are found ordered in a tetrahedral pair. The fundamental unit can be conceptualized as Mg(2)-B-P sheets sandwiching Mg(1) octahedra that do not share polyhedral elements with each other but bridge the Mg(2)-B-P sheets. These T_2M-M-T_2M units (T = tetrahedral, M = octahedral) are repeated along **b** with H bonds spanning the spaces between units.

The fundamental cluster in the T_2M sheets is a Mg(2) octahedron sharing the vertices at either end of one of its equatorial edges (i.e., the edges roughly parallel to the **ac** plane) with a B and P tetrahedral pair (Fig. 1). The remaining basal vertex of each of the two tetrahedra is shared with a neighboring Mg(2) octahedron in the sheet. Thus, orderly rows and columns parallel to **a** and **c** are formed by the repeat of the cluster. Parallel to the **a** direction in a T_2M sheet the Mg(2) octahedra are connected by B tetrahedra, and octahedra are connected by P tetrahedra parallel to **c**.

All of the apices of the tetrahedra in a T_2M sheet point into the middle of the T_2M-M-T_2M unit. Each Mg(1) octahedron in the middle of a T_2M-M-T_2M unit shares two vertices of one of its equatorial edges (i.e., the edges shared with the T_2M sheets) with the two apices of a B-P tetrahedral pair of one T_2M sheet (Fig. 2). The remaining two equatorial vertices of each Mg(1) octahedron are shared with the two apices of a B-P tetrahedral pair in the other T_2M sheet. The apices of the Mg(1) octahedra are not positioned midway between the T_2M sheets of a T_2M-M-T_2M unit. One apex is closer to one of the T_2M sheets, and the other apex is closer to the other sheet of the unit. Thus, the Mg(1) octahedra are slanted between the opposing T_2M sheets.

One T_2M sheet of a unit may be obtained from the other by inversion of each Mg(2)-B-P cluster through its bridging Mg(1) because the Mg(1) site is a center of symmetry. The center of symmetry operation results in each Mg(2) octahedron of one T_2M sheet overlying (along **b***) the void between four Mg(2)-B-P clusters in the other T_2M sheet. (Notice the voids in the sheet shown in Fig. 1.)

The arrangement of Mg(1) octahedra, bridging the space between opposing T_2M sheets but not sharing polyhedral

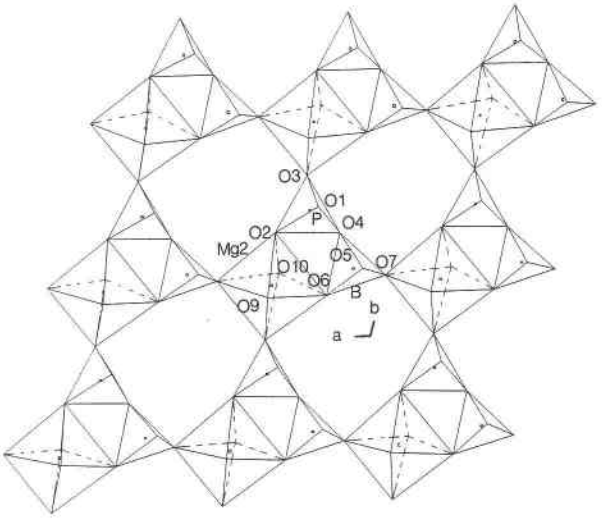

Fig. 1. The T_2M sheet of lüneburgite at ¾ along **b**. The **a** and **c** directions are indicated, but note that in this figure their intersection is not placed at the cell origin.

elements with each other, forms two intersecting channels in each T_2M-M-T_2M unit (Fig. 3). One channel is parallel to **a** and the other to **c**. They are topologically similar and have a minimum diameter, excluding H bonds, of about 4 Å. Some of the strong O-H bonds protrude into these channels, and some H bonds obliquely cross the channels. The channels are formed by a spiraling series of linked polyhedra with a repeat of B-Mg(1)-P-Mg(2).

The apices of each Mg(1) and Mg(2) octahedron, which are not shared with other coordination polyhedra, are anchored by H bonds to adjacent structural elements.

The twinning observed in the studied material (a 180° rotation about [1$\bar{1}$0]) is growth twinning. The twin plane cuts obliquely across the H-bonded gap between T_2M-M-T_2M units.

POLYHEDRAL DISTORTIONS

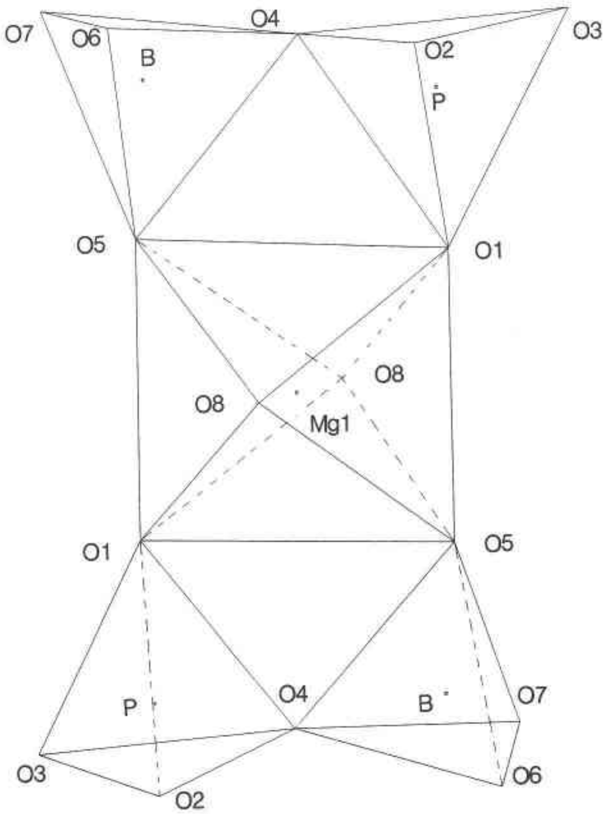

Fig. 2. The Mg(1) octahedron bridging the T_2M sheets of a T_2M-M-T_2M unit in lüneburgite. The **b** axis passes parallel and very close to a line connecting the two O(4) atoms shown.

The bond lengths, edge lengths, and bond angles of the four polyhedral elements are given in Table 5. The Mg(1) octahedra are distorted, the bonds to the apical O atoms [O(8) H_2O] being longer (2.229 Å) than the bonds to the equatorial O atoms, and the latter being of unequal length (2.010 and 2.054 Å). The mean octahedral quadratic elongation, $\langle\lambda_{\mathrm{oct}}\rangle$, is 1.005, and the variance of the octahedral angles (Robinson et al., 1971), $\sigma_{\theta(\mathrm{oct})^2}$, is $3.9^{\circ 2}$ (both calculated with the program Volcal by Hazen and Finger, 1982). Thus, Mg(1) is slightly elongated in the apical directions, and the equatorial O atoms form the corners of

TABLE 4b. Lüneburgite: anisotropic thermal parameters, U_{ij} (× 100)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg(1)	1.18(3)	0.83(3)	1.00(3)	0.129(21)	0.069(22)	−0.205(21)
Mg(2)	0.873(24)	1.036(25)	0.676(23)	−0.013(16)	0.242(16)	−0.095(16)
P	0.823(19)	0.785(19)	0.529(19)	0.073(11)	0.133(12)	−0.070(11)
B	0.70(5)	0.77(5)	0.76(5)	−0.01(4)	0.10(4)	−0.21(4)
O(1)	1.49(4)	0.85(4)	1.10(4)	0.18(3)	−0.06(3)	−0.27(3)
O(2)	1.07(4)	1.78(5)	0.89(4)	0.10(3)	0.38(3)	−0.19(3)
O(3)	1.54(4)	1.04(4)	0.61(4)	0.24(3)	0.16(3)	−0.03(3)
O(4)	0.90(4)	1.23(4)	0.74(4)	−0.12(3)	−0.08(3)	0.05(3)
O(5)	1.15(4)	0.92(4)	1.64(4)	0.15(3)	−0.09(3)	−0.26(3)
O(6)	1.07(4)	1.90(5)	1.08(4)	−0.14(3)	0.42(3)	−0.55(3)
O(7)	0.73(4)	0.96(4)	1.42(4)	−0.14(3)	0.23(3)	−0.36(3)
O(8)	1.96(5)	1.85(5)	1.87(5)	−0.12(4)	0.76(4)	−0.06(4)
O(9)	1.63(5)	1.18(4)	1.05(4)	0.09(3)	0.21(3)	−0.10(3)
O(10)	1.23(4)	1.36(4)	1.28(4)	0.09(3)	0.45(3)	0.22(3)

Note: The U_{ij} values are coefficients in the expression $\exp[-\Sigma_{ij}U_{ij}h_ih_j]$. Estimated standard errors refer to the last digit.

TABLE 5. Bond distances (Å) and angles of lüneburgite

			Mg(1) octahedron		
Mg(1)	−O(1)a	2.010(1)	O(1)a-O(5)a	2 × 2.948(1)	2 × 93.0(1)
	−O(1)b	2.010(1)	O(1)a-O(5)b	2 × 2.798(1)	2 × 87.0(1)
	−O(5)a	2.054(1)	O(1)a-O(8)a	2 × 2.974(1)	2 × 89.0(1)
	−O(5)b	2.054(1)	O(1)a-O(8)b	2 × 3.028(1)	2 × 91.0(1)
	−O(8)a	2.229(1)	O(5)a-O(8)a	2 × 3.008(1)	2 × 89.1(1)
	−O(8)b	2.229(1)	O(5)a-O(8)b	2 × 3.054(2)	2 × 90.9(1)
Mean		2.098		2.968	90.0
			Mg(2) octahedron		
Mg(2)	−O(2)	2.080(1)	O(2)-O(6)	3.079(1)	94.7(1)
	−O(3)c	2.040(1)	O(2)-O(7)d	2.950(1)	90.5(1)
	−O(6)	2.105(1)	O(2)-O(9)	2.860(1)	86.3(1)
	−O(7)d	2.071(1)	O(2)-O(10)	3.015(1)	92.3(1)
	−O(9)	2.100(1)	O(3)c-O(6)	2.888(1)	88.3(1)
	−O(10)	2.100(1)	O(3)c-O(7)d	2.767(2)	86.6(1)
			O(3)c-O(9)	2.914(1)	89.5(1)
			O(3)c-O(10)	2.979(1)	92.0(1)
			O(6)-O(9)	2.948(1)	89.0(1)
			O(6)-O(10)	2.870(1)	88.6(1)
			O(7)d-O(9)	3.023(1)	92.9(1)
			O(7)d-O(10)	2.940(1)	89.7(1)
Mean		2.083		2.941	90.0
			P tetrahedron		
P	−O(1)	1.529(1)	O(1)-O(2)	2.510(1)	110.2(1)
	−O(2)	1.531(1)	O(1)-O(3)	2.524(1)	112.0(1)
	−O(3)	1.516(1)	O(1)-O(4)	2.520(1)	108.9(1)
	−O(4)	1.568(1)	O(2)-O(3)	2.517(1)	111.4(1)
			O(2)-O(4)	2.516(1)	108.6(1)
			O(3)-O(4)	2.457(1)	105.6(1)
Mean		1.536		2.507	109.5
			B tetrahedron		
B	−O(4)	1.492(1)	O(4)-O(5)	2.407(1)	108.7(1)
	−O(5)	1.470(1)	O(4)-O(6)	2.403(1)	107.9(1)
	−O(6)	1.481(1)	O(4)-O(7)	2.383(1)	108.1(1)
	−O(7)	1.451(1)	O(5)-O(6)	2.421(1)	110.2(1)
			O(5)-O(7)	2.397(1)	110.3(1)
			O(6)-O(7)	2.425(1)	111.6(1)
Mean		1.474		2.406	109.5

Note: Standard deviations of the last digit are in parentheses. For angles read O(4)-B(1)-O(5) etc. Symmetry codes: a = *x*, −1 + *y*, *z*; b = −*x*, 1 − *y*, −*z*; c = *x*, *y*, −1 + *z*; d = 1 + *x*, *y*, *z*; e = *x*, 1 + *y*, *z*; f = *x*, *y*, 1 + *z*; g = −1 + *x*, *y*, *z*.

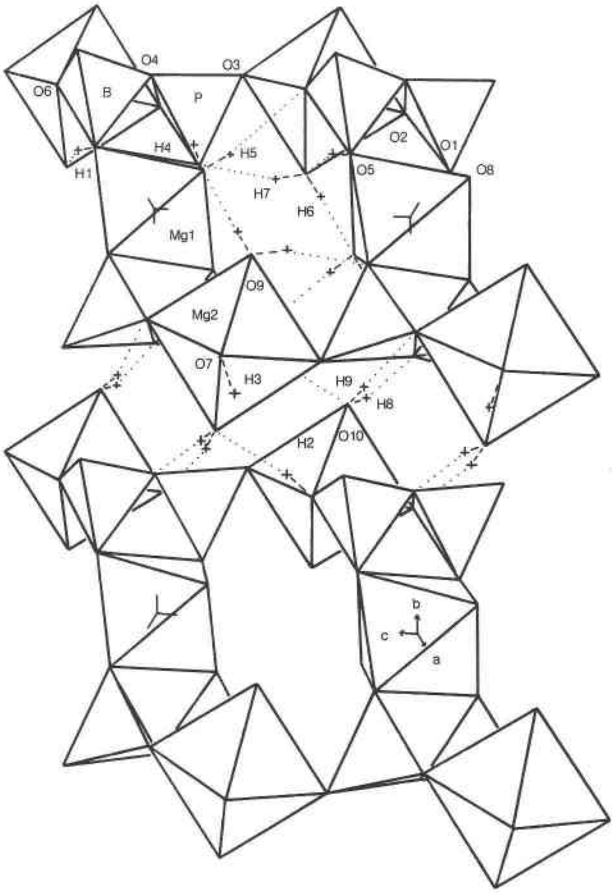

Fig. 3. A perspective drawing of lüneburgite from −½ to +½ on **a** showing the repeated T_2M-M-T_2M units along **b**, the channel parallel to **a**, the strong H-O bonds (dashed), H bonding (dotted), and the presence of only H bonds between units.

a parallelogram rather than a square. The mean Mg(1)-O bond length, 2.098 Å, is typical for Mg. The data of Shannon and Prewitt (1969) yield 2.08 and 2.10 Å for $^{[6]}$Mg-$^{[2]}$O and $^{[6]}$Mg-$^{[3]}$O, respectively.

The Mg(2) octahedron has bonds ranging from Mg(2)-O = 2.040 to 2.105 Å with a mean of 2.083 Å. The values of $\langle\lambda_{\text{oct}}\rangle$ and $\sigma_{\theta(\text{oct})^2}$ for this site are 1.002 and 6.5$^{\circ 2}$, respectively, reflecting the fact that the apical bond lengths are nearly the same as the equatorial bond lengths but the octahedral angles vary from 90°.

The mean P-O distance, 1.536 Å, falls well within the range known for P in orthophosphates and compares closely to P-O in seamanite, 1.534 Å (Moore and Ghose, 1971). The mean bond length for $BO(OH)_3$, 1.474 Å, falls between that of BO_4 in sinhalite, 1.489 Å (Fang and Newnham, 1965), and that of $B(OH)_4$ in seamanite, 1.466 Å (Moore and Ghose, 1971).

STRUCTURAL H_2O, OH IONS, AND H BONDING

H(1), H(2), and H(3) form OH ions with the O(5), O(6), and O(7) vertices, respectively, of each B tetrahedron. Only the O(4) vertex of B, shared with P, is not a OH ion. None of the four vertices of the P tetrahedron, which of course includes O(4), is a OH ion. H(1) forms a H bond with O(9), linking the B tetrahedron and Mg(2) octahedron of each Mg(2)-P-B cluster (Fig. 4a). H(2) is H bonded to the O(10) vertex of a Mg(2) octahedron in an adjacent T_2M-M-T_2M unit (Fig. 4b). H(3) forms a H bond with the O(3) vertex of P in an adjacent T_2M-M-T_2M unit (Fig. 4c).

Structural H_2O occurs at O(8), O(9), and O(10), which are the unshared apices of the octahedra. The unshared apices of the Mg(1) octahedra [O(8)] are H bonded to vertices in the Mg(2)-B-P clusters of the T_2M sheets. The H atoms in each O(8) H_2O are H(4) and H(5). H(4) is H bonded to the O(2) vertex of a P tetrahedron, and H(5) is H bonded to the O(6) vertex of a B tetrahedron (Fig. 4d). The unshared apex of Mg(2) pointing into the center of a T_2M-M-T_2M unit, O(9), is H bonded to a Mg(1) octahedron, and the unshared apex pointing into the gap between T_2M-M-T_2M units, O(10), is H bonded to clusters in an adjacent unit. With respect to the H atoms of the O(9) H_2O, H(6) is H bonded to the closest O(8) vertex of an adjacent Mg(1) octahedron, and H(7) is H bonded

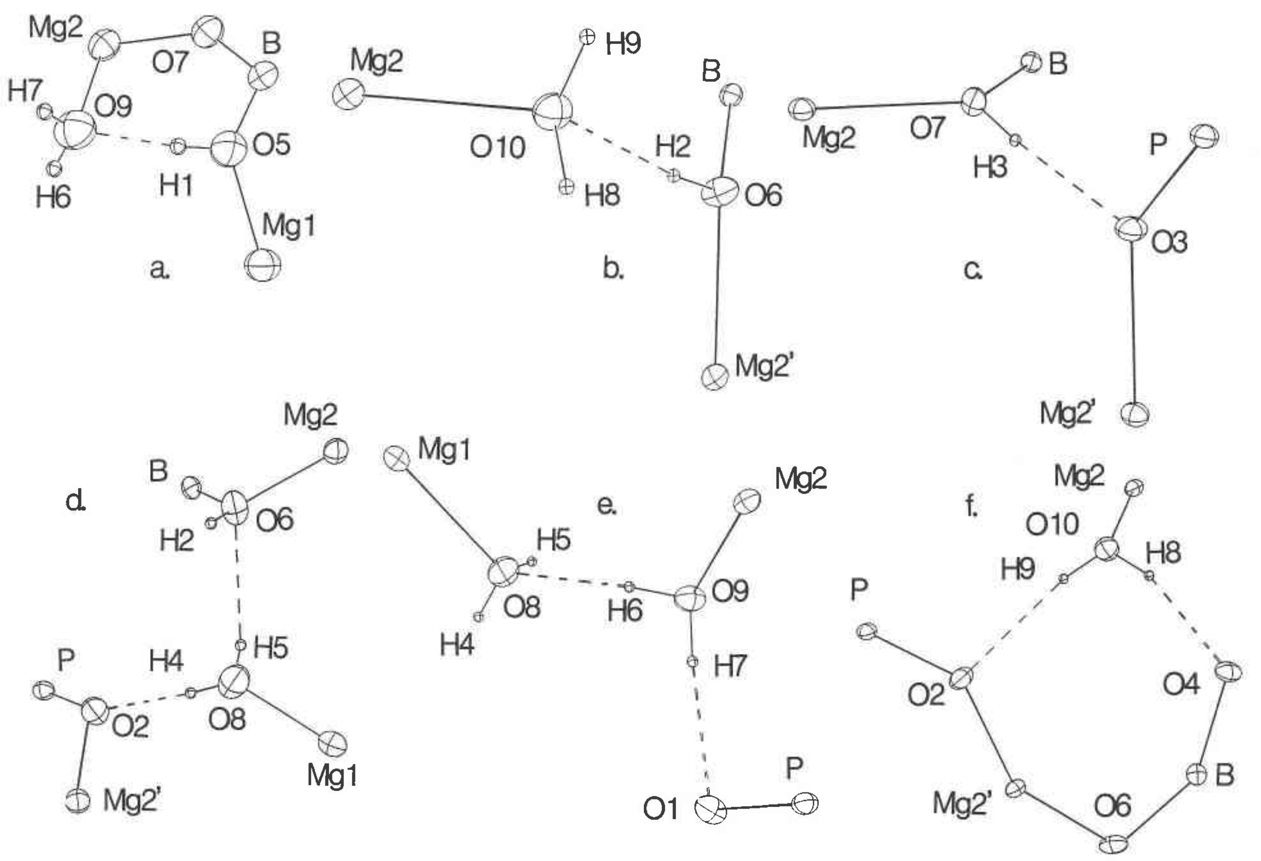

Fig. 4. The H bonds. (**a**) H(1) · · · O(9), (**b**) H(2) · · · O(10), (**c**) H(3) · · · O(3), (**d**) H(4) · · · O(2) and H(5) · · · O(6), (**e**) H(6) · · · O(8) and H(7) · · · O(1), (**f**) H(8) · · · O(4) and H(9) · · · O(2).

to the O(1) vertex of the P tetrahedron of an adjacent Mg(2)-B-P cluster (Fig. 4e). H(8) and H(9) are the H atoms of the O(10) H_2O. H(9) is H bonded to O(2), an equatorial vertex of an Mg(2) octahedron in an adjacent T_2M-M-T_2M unit. H(8) is H bonded to the O(4) vertex of a B tetrahedron of a different Mg(2)-B-P cluster in an adjacent T_2M-M-T_2M unit (Fig. 4f).

Adjacent T_2M-M-T_2M units along the **b** axis are only connected by the H bonds H(2) · · · O(10), H(3) · · · O(3), H(8) · · · O(4), and H(9) · · · O(2). It might be supposed that with H bonding alone between T_2M-M-T_2M units in lüneburgite, the {010} cleavage would be perfect. Yet examination of the crystals with the binocular microscope reveals this cleavage to be only fair. The probable explanation lies in the fact that the T_2M sheet surface is not flat. The apices of Mg(2) octahedra project from the T_2M-M-T_2M unit surfaces beyond the level of the basal faces of the B and P tetrahedra (Fig. 3). Because of the center of symmetry in lüneburgite, the recesses in the surface of a T_2M sheet (i.e., where the basal faces of the tetrahedra are) coincide with the projecting apices of Mg(2) octahedra of the T_2M sheet of the adjacent T_2M-M-T_2M unit. Thus, the T_2M-M-T_2M unit surfaces, in a sense, mate with each other in a saw-toothed fashion though only bonded by H bonds.

As a test of the H bond assignments, bond-valence calculations were carried out for lüneburgite (method of Brown, 1981; Brown and Altermatt, 1985). H coordinates are known to be poorly determined by X-ray diffraction. At the suggestion of I. D. Brown (personal communication, 1990), we assumed (1) a strong O-H bond distance of 0.96 Å (as would be expected from neutron diffraction) and (2) a valence sum of 1.00 for each H atom (and thus the calculation of the strong O-H bond valence by difference). The results are given in Table 6. Even with the above corrections, the valence sums for O(1) and O(3) suggest that these atoms are undersaturated (1.92 and 1.91) and that O(8) through O(10) are oversaturated (2.16, 2.16, and 2.10). These slight differences might indicate that the O(5)-H(1) · · · O(9), O(6)-H(2) · · · O(10), and O(9)-H(6) · · · O(8) H bonds described above are not oriented directly at the proposed O atoms but rather are directed somewhere between O atoms O(1) and O(3). The deviation from 180° of many of the O-H · · · O angles in lüneburgite (Table 7) demonstrates that some of the H bonds are not directly oriented at individual O atom positions.

COMPARISON TO SEAMANITE

Seamanite, $Mn_3^{2+}(OH)_2PO_4B(OH)_4$, the only other borate-phosphate thus far described, belongs to a complete-

TABLE 6. Bond valences for lüneburgite

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)	Σ
Mg(1)	2 × 0.41				2 × 0.37			2 × 0.24			2.04
Mg(2)		0.35	0.38			0.33	0.36		0.33	0.33	2.08
P	1.29	1.28	1.34	1.15							5.06
B				0.71	0.75	0.73	0.80				2.99
H(1)					0.82				0.18		1.00
H(2)						0.85				0.15	1.00
H(3)			0.19				0.81				1.00
H(4)		0.13						0.87			1.00
H(5)						0.08		0.92			1.00
H(6)								0.13	0.87		1.00
H(7)	0.22								0.78		1.00
H(8)				0.19						0.81	1.00
H(9)		0.19								0.81	1.00
Σ	1.92	1.95	1.91	2.05	1.94	1.99	1.97	2.16	2.16	2.10	

Note: H bond valence sums are assumed to equal 1.00.

ly different structure type than lüneburgite. As described by Moore and Ghose (1971), the fundamental structural feature of seamanite is a chain of face-sharing Mn-O,OH octahedral trimers laterally linked by PO_4 and $B(OH)_4$ tetrahedra. This chain runs parallel to **c** in seamanite, a mineral with an acicular crystal habit. In contrast, the fundamental unit in lüneburgite, a mineral forming tabular, blocky, and flakelike crystals and having a fair {010} cleavage, is the layered T_2M-M-T_2M unit.

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TABLE 7. H bond distances (Å), angles, and H · · · OH of lüneburgite

H1	–O(5)H	0.81(2)	O5—H1	O9W	2.787(1)	169.4(2.0)	H1 . . . O9 = 1.987
H2	–O(6)H	0.84(3)	O6—H2	O10W	2.870(1)	170.8(2.3)	H2 . . . O10 = 2.036
H3	–O(7)H	0.82(2)	O7W—H3	O3	2.767(1)	176.8(2.0)	H3 . . . O3 = 1.951
H4	–O(8)W	0.87(2)	O8W—H4	O2	2.947(1)	173.0(2)	H4-O8W-H5 106.4(1) H4 . . . O2 = 2.082
H5	–O(8)W	0.78(3)	O8W—H5	O6	3.258(1)	176.9(2)	H5 . . . O6 = 2.494
H6	–O(9)W	0.81(2)	O9W—H6	O8	2.919(1)	176.7(2)	H6-O9W-H7 102.5(1) H6 . . . O8 = 2.111
H7	–O(9)W	0.80(2)	O9W—H7	O1	2.660(1)	162.0(2)	H7 . . . O1 = 1.888
H8	–O(10)W	0.81(2)	O10W—H8	O4	2.754(1)	158.5(2)	H8-O10W-H9 108.6(1) H8 . . . O4 = 1.983
H9	–O(10)W	0.81(3)	O10W—H9	O2	2.756(1)	170.8(2)	H9 . . . O2 = 1.949

Note: Standard deviations of the last digit are in parentheses.

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