Refinement of the structure of hemimorphite

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Auszug

Die Kristallstruktur von Kieselzinkerz $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ wurde neu bestimmt auf Grund von dreidimensionalen Intensitätswerten, die sowohl photographisch als auch mit dem Zählrohr gefunden wurden. Die photographischen Werte führten zu $R = 0{,}071$, die mit dem Zählrohr gemessenen zu $R = 0{,}040$. Die aus beiden Messungen folgenden Si—O-Abstände (im Mittel 1,627 Å) und Si—O—Si-Winkel (150°) unterscheiden sich nicht merklich. Die Zn—O-Abstände (im Mittel 1,954 Å) haben beträchtlich kovalenten Charakter. Dem Vorschlag Zoltais folgend, wird die Struktur als dreidimensionales Tetraedergerüst beschrieben. Das Wassermolekül zeigt starke Wärmeschwingung und könnte zum Teil ungeordnet sein.

Abstract

The structure of hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ has been redetermined with three-dimensional data obtained both photographically and with a counter-diffractometer. R values of 7.1% and 4.0% were obtained for the two sets of data. There are no significant differences between the Si—O bond lengths (mean 1.627 Å) and the Si—O—Si angle is 150°. The Zn—O bonds (mean length 1.954 Å) show considerable covalent character. Following Zoltai, the structure is described as a three-dimensional framework of tetrahedra. The water molecule shows large thermal vibrations and may be partly disordered.

Introduction

Hemimorphite is a zinc silicate mineral of empirical formula $Zn_2SiO_4 \cdot H_2O$. Ito and West[1] studied the crystal structure and showed that it contained Si_2O_7 groups, and that the formula should be written $Zn_4Si_2O_7(OH)_2 \cdot H_2O$. A redetermination of the structure

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[1] T. Ito and J. West, The structure of hemimorphite. Z. Kristallogr. **83** (1932) 1—8.

by Barclay and Cox[2], using two-dimensional data for two projections, indicated an Si—O—Si angle of 133° and an unusually long Si—O bridge bond of 1.72 Å. These results were not of great accuracy, however, because of overlap and the absence of a centre of symmetry in the (100) projection[3]. Because of the interest in d—p π-bonding in silicon-oxygen bonds, and the light thrown on this by the observed variations in bond lengths and angles[4], we decided to undertake a three-dimensional study of hemimorphite.

Experimental

Crystal data

Hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, $M = 481.7$. Orthorhombic, $a = 8.370, b = 10.719, c = 5.120$ Å, $V = 459.4$ Å^3, $Z = 2, D_c = 3.482$. $F(000) = 464$. Space group $Imm2$. The material used in the present study was from the same batch as used by Barclay and Cox.

The cell dimensions were measured earlier by Gossner and Mussgnug[5], by Ito and West[1], by Swanson and Fuyat[6], and by Barclay and Cox[2]. In this work they were remeasured from zero-layer precession photographs, and on a Hilger linear diffractometer[7].

Table 1. *Unit-cell dimensions of hemimorphite*

Determination	a	b	c
Gossner and Mussgnug	8.43 Å	10.75 Å	5.15 Å
Ito and West	8.40	10.72	5.12
Barclay and Cox	8.37	10.67	5.10
Swanson and Fuyat	8.370	10.719	5.120
Precession data	8.369	10.728	5.116
Diffractometer	8.373	10.718	5.120

[2] G. A. Barclay and E. G. Cox, The structure of hemimorphite. Z. Kristallogr. 113 (1960) 23—29.

[3] D. W. J. Cruickshank, H. Lynton and G. A. Barclay, A reinvestigation of the crystal structure of thortveitite $Sc_2Si_2O_7$. Acta Crystallogr. 15 (1962) 491—498.

[4] D. W. J. Cruickshank, The role of $3d$-orbitals in π-bonds between (a) silicon, phosphorus, sulphur, or chlorine and (b) oxygen or nitrogen. J. Chem. Soc. (1961) 5486—5504.

[5] B. Gossner und F. Mussgnug, Vergleichende röntgenographische Untersuchung von Silikaten. Z. Kristallogr. 70 (1929) 171—184.

[6] H. E. Swanson and R. K. Fuyat, Standard x-ray diffraction powder patterns. National Bureau of Standards circular 539, Vol. II (1953) 62—63.

[7] U. W. Arndt and D. C. Phillips, The linear diffractometer. Acta Crystallogr. 14 (1961) 807—818.

The values obtained were in close agreement with those of Swanson and Fuyat, and their more accurate values were used in this analysis. The various determinations are listed in Table 1, with kX values converted to Å for the first two determinations.

Three-dimensional data were obtained by visual estimation of equi-inclination Weissenberg photographs of the reciprocal-lattice layers $hk\bar{1}$ to $hk7$, taken with MoKα radiation. The crystal used had approximate dimensions $0.02 \times 0.06 \times 0.2$ mm, with the longest dimension parallel to the rotation axis. Corrections for Lorentz and polarization factors were applied using a Pegasus computer programme written by J. G. F. Smith. No corrections were made for absorption. The measurements gave 651 $F(hkl)$, including the $hk\bar{1}$ layer, which should only differ from the $hk1$ layer by the effects of anomalous dispersion.

A second set of data, covering layers $hk0$ to $hk7$, was obtained on the linear diffractometer[7] from another crystal of similar dimensions. The diffractometer had a scintillation counter and used balanced Sr and Zr filters with MoKα radiation. The data were corrected for Lorentz and polarization factors with a DEUCE computer programme written by J. G. Sime, giving 387 independent $F(hkl)$ on a single scale.

Refinement

Initial refinements from the parameters of Barclay and Cox[2], using both sets of data in separate least-squares calculations, were carried out with the DEUCE computer programme of J. S. Rollett[8]. The final refinements, with allowance for the real and imaginary components of the anomalous dispersion for Zn and Si, were done with the KDF 9 structure-factor least-squares programme of J. G. F. Smith and D. W. J. Cruickshank. For Zn the imaginary component of anomalous dispersion, $\Delta f'' = 1.5$, and for Si $\Delta f'' = 0.1$. Coordinates and anisotropic vibration parameters were refined together with an overall scale factor in the case of the diffractometer data. For the photographic data, consisting of nine reciprocal lattice layers obtained about the same rotation axis, separate scale factors for each layer were refined. With this procedure the data determine only the relative values of the vibration components in the direction of the rotation

[8] J. S. Rollett, General programs for crystal structure analysis on the English Electric Deuce computer. "Computing methods and the phase problem in x-ray analysis", Ed. Ray Pepinsky, J. M. Robertson and J. C. Speakman (Pergamon Press, London, 1961) 87—101.

axis[9], and therefore the U_{33} value of the zinc atom was held fixed. In the final cycles the weighting schemes were

$$w = 1/(12 + F_0 + 0.01\ F_0{}^2)$$

for the photographic data, and

$$w = \left\{1 - \exp\left[-3\left(\frac{\sin\theta}{\lambda}\right)^2\right]\right\} \Big/ (1 + 10^{-6}\ F_0{}^3)$$

for the diffractometer data.

As the space group is polar, the effect of anomalous dispersion is to produce differences between corresponding reflections hkl and $hk\bar{l}$. Since we did not know initially whether the photographic data, for instance, were $hk\bar{1}$ to $hk7$ or $hk1$ to $hk\bar{7}$, two parallel refinements with

Table 2. *Final fractional coordinates and estimated standard deviations.*
First value from photographic data. Second value from diffractometer data.
Third value is weighted mean

	x	y	z
Zn	0.2043(1)	0.1611(1)	0
	0.2044(1)	0.1612(1)	0
	0.2044(1)	0.1612(1)	0
Si	0	0.1474(4)	0.5083(20)
	0	0.1463(3)	0.5054(15)
	0	0.1467(2)	0.5064(11)
O(1)	0.1585(10)	0.2089(8)	0.6370(23)
	0.1590(7)	0.2067(6)	0.6378(15)
	0.1588(6)	0.2075(5)	0.6375(12)
O(2)	0	0.1687(11)	0.1906(28)
	0	0.1656(10)	0.1909(19)
	0	0.1671(7)	0.1908(16)
O(3)	0.3088(16)	0	1.0396(59)
	0.3071(14)	0	1.0356(33)
	0.3077(11)	0	1.0365(28)
O(4)	0	0	0.5816(52)
	0	0	0.5896(29)
	0	0	0.5877(25)
O(5)	$\frac{1}{2}$	0	0.5051(114)
	$\frac{1}{2}$	0	0.5068(149)
	$\frac{1}{2}$	0	0.5053(92)

[9] E. C. LINGAFELTER and JERRY DONOHUE, Degeneracy between interlayer scale factors and b_{ij} in structure refinement. Acta Crystallogr. **20** (1966) 321.

opposite polarities were carried out with each set of data. We then discovered that the reversal of polarity did not lead to any marked differences in the agreement indices (especially with the diffractometer data), but did produce very significantly different z coordinates for the zinc atom relative to the light atoms. It was evident that the phase change on scattering by an "anomalous" atom could be closely simulated by a change of its polar coordinate. TEMPLETON et al.[10] have recently pointed out that this effect is to be expected generally in any polar space group.

With the diffractometer data the final R values $(R = \Sigma\Delta/\Sigma k|F_o|)$ were $4.21^0/_0$ and $4.03^0/_0$ for the two polarities, and the R' values $(R' = \Sigma\Delta^2/\Sigma wk^2|F_o|^2)$ were 0.0026 and 0.0025. Relative to the light atoms, the zinc positions differed however by about 0.05 Å. According to HAMILTON's significance tests[11] the slight differences in the residuals are in fact significant at the $0.5^0/_0$ level.

Table 3.

Anisotropic vibration parameters and their estimated standard deviations ($Å^2$)
First value is from photographic data. Second value is from diffractometer data

	U_{11}	U_{22}	U_{33}	$2\,U_{23}$	$2\,U_{31}$	$2\,U_{12}$
Zn	0.013(1)	0.016(1)	0.016(0)	$-0.002(2)$	$-0.004(2)$	$-0.005(1)$
	0.008(1)	0.012(1)	0.012(1)	0.001(1)	0.002(1)	$-0.005(1)$
Si	0.012(1)	0.014(1)	0.009(2)	0.000(5)	0	0
	0.005(1)	0.009(1)	0.009(1)	$-0.002(4)$	0	0
O(1)	0.013(3)	0.020(3)	0.021(5)	0.017(7)	$-0.012(7)$	$-0.024(6)$
	0.005(2)	0.020(3)	0.015(3)	0.003(5)	$-0.002(4)$	$-0.013(5)$
O(2)	0.012(4)	0.017(5)	0.015(7)	0.003(9)	0	0
	0.007(4)	0.024(5)	0.016(4)	$-0.006(6)$	0	0
O(3)	0.029(6)	0.014(4)	0.050(22)	0	0.000(14)	0
	0.025(5)	0.009(4)	0.037(12)	0	$-0.017(9)$	0
O(4)	0.022(7)	0.018(6)	0.031(12)	0	0	0
	0.014(6)	0.011(5)	0.016(5)	0	0	0
O(5)	0.070(19)	0.191(46)	0.009(12)	0	0	0
	0.040(12)	0.140(29)	0.062(20)	0	0	0

[10] TATZUO UEKI, ALLAN ZALKIN and DAVID H. TEMPLETON, Crystal structure of thorium nitrate pentahydrate by x-ray diffraction. Acta Crystallogr. 20 (1966) 836—841.

[11] WALTER C. HAMILTON, Significance tests on the crystallographic R factor. Acta Crystallogr. 18 (1965) 502—510.

Table 4. *Observed and calculated structure factors for diffractometer data*

h	k	l	F_o	F_c
0	1	1	77.5	85.5
0	3	1	131.2	144.7
0	3	3	113.4	120.2
0	3	5	70.7	78.1
0	4	0	91.5	101.7
0	4	2	102.1	107.2
0	4	4	90.8	95.3
0	4	6	49.1	55.5
0	5	1	50.1	54.1
0	5	3	66.9	69.0
0	6	0	205.1	227.7
0	6	2	154.5	166.4
0	6	4	111.8	114.4
0	6	6	70.6	72.1
0	7	1	88.9	91.6
0	7	3	39.3	40.6
0	7	7	20.2	26.9
0	8	0	11.8	16.8
0	8	4	13.4	14.1
0	8	6	11.7	13.7
0	9	1	100.5	102.1
0	9	3	61.5	60.9
0	9	7	37.6	36.3
0	10	0	76.8	77.4
0	10	2	85.3	84.0
0	10	4	77.4	76.2
0	10	6	47.5	45.6
0	11	1	34.3	34.5
0	11	3	25.2	25.1
0	11	5	19.5	21.8
0	11	7	15.2	14.0
0	12	0	77.3	77.9
0	12	2	73.1	72.2
0	12	4	60.9	60.0
0	13	1	49.7	48.8
0	13	3	36.9	36.2
0	13	5	27.5	30.6
1	0	1	12.5	10.9
1	0	3	31.0	34.1
1	1	2	35.1	35.9
1	1	4	18.7	24.3
1	2	1	11.4	12.3
1	2	3	13.2	14.2
1	2	5	7.0	9.5
1	3	0	146.2	148.5
1	3	2	76.4	75.7
1	3	4	55.2	58.0
1	4	1	29.6	28.1
1	4	3	12.2	13.0
1	4	5	5.4	7.2
1	5	0	40.4	38.9
1	5	2	21.6	21.7
1	5	4	7.1	8.4
1	6	1	16.3	17.2
1	6	3	18.3	16.4
1	6	5	16.7	18.0
1	7	0	48.8	49.7
1	7	2	45.4	45.8
1	7	4	39.1	40.1
1	7	6	21.1	21.5
1	8	1	26.4	27.5
1	8	3	18.8	19.9
1	8	5	14.6	14.5
1	9	0	42.0	42.7
1	9	2	32.8	34.9
1	9	4	35.1	35.4
1	9	6	22.6	21.7
1	10	1	10.9	13.3
1	10	3	7.6	7.6
1	11	0	10.0	9.3
1	11	2	11.0	12.3
1	11	4	9.9	10.3
1	12	1	20.2	20.3
1	12	3	9.3	9.4
1	13	0	29.9	30.2
1	13	2	26.9	24.5
1	13	4	20.8	20.6
1	14	1	22.8	22.3
2	0	0	133.8	126.1
2	0	4	69.5	70.2
2	1	1	155.8	147.4
2	1	3	107.8	104.6
2	1	5	46.6	50.9
2	2	0	80.9	75.5
2	2	2	65.2	59.1
2	2	4	26.6	26.2
2	2	6	20.0	22.2
2	3	1	150.3	151.4
2	3	3	153.9	152.9
2	3	5	87.1	88.8
2	4	0	50.2	48.7
2	4	2	62.8	61.1
2	4	4	36.0	33.9
2	4	6	20.2	19.5
2	5	1	56.8	55.8
2	5	3	51.1	50.8
2	5	5	20.3	20.6
2	6	0	91.9	92.9
2	6	2	102.1	102.4
2	6	4	64.6	65.1
2	6	6	41.4	39.8
2	7	1	123.1	125.9
2	7	3	87.3	88.8
2	7	5	52.0	53.2
2	7	7	34.3	38.9
2	8	0	37.7	37.3
2	8	2	32.4	32.8
2	8	4	16.4	18.8
2	9	1	84.8	86.1
2	9	3	77.3	77.7
2	9	5	50.7	52.2
2	10	0	31.4	31.8
2	10	2	40.9	40.2
2	10	4	30.4	27.9
2	10	6	11.1	17.1
2	11	3	3.5	4.1
2	12	0	51.2	51.6
2	12	2	62.5	60.2
2	12	4	47.8	46.7
2	12	6	32.8	28.6
2	13	1	67.1	66.0
2	13	3	54.4	52.6
3	0	1	146.9	141.6
3	0	3	163.2	157.2
3	0	5	82.9	80.6
3	1	0	36.0	35.2
3	1	2	48.4	45.0
3	1	4	29.7	28.4
3	2	1	77.4	73.8
3	2	3	90.5	88.7
3	2	5	45.7	43.0
3	2	7	15.2	17.2
3	3	0	137.6	132.4
3	3	2	110.9	106.1
3	3	4	46.9	46.1
3	3	6	40.2	37.9
3	4	1	124.8	122.4
3	4	3	88.7	86.5
3	4	5	55.1	54.1
3	4	7	37.5	38.4
3	5	0	53.4	52.5
3	5	2	36.0	33.1
3	5	4	20.2	18.0
3	6	1	111.7	113.4
3	6	3	101.3	100.2
3	6	5	58.3	58.4
3	6	7	39.9	42.6
3	7	2	47.6	47.9
3	7	4	35.2	34.4
3	7	6	13.9	12.9
3	8	1	16.4	16.5
3	8	3	23.7	24.0
3	9	0	61.2	62.2
3	9	2	74.3	74.6
3	9	4	50.8	50.9
3	10	1	81.1	82.2
3	10	3	56.9	58.4
3	10	5	40.6	42.5
3	10	7	34.2	34.8
3	11	0	13.0	13.5
3	11	2	19.9	21.4
3	11	4	17.0	19.2
3	12	1	53.4	53.3
3	12	3	36.7	36.6
3	12	5	27.3	27.4
3	13	0	15.4	15.0
3	13	2	25.0	25.7
4	0	0	131.0	123.6
4	0	2	103.3	97.4
4	0	4	82.3	78.2
4	0	6	42.5	41.8
4	1	1	13.1	13.5
4	1	3	10.4	8.5
4	1	5	12.5	12.5
4	2	0	7.9	9.5
4	2	2	32.1	30.9
4	2	6	16.5	17.4
4	3	1	69.0	65.3
4	3	3	10.9	10.8
4	3	5	24.7	21.2
4	3	7	9.1	10.8
4	4	0	75.1	72.6
4	4	2	49.8	48.2
4	4	4	43.8	42.3
4	4	6	33.2	33.3
4	5	1	30.9	30.1
4	5	3	7.9	2.9
4	5	5	15.1	14.6
4	6	0	97.4	95.0
4	6	2	65.3	64.4
4	6	4	50.9	48.0
4	6	6	32.9	32.6
4	7	1	9.0	10.4
4	7	3	18.7	18.3
4	7	5	11.5	10.8
4	8	0	11.7	11.8
4	8	2	8.6	11.1
4	9	1	29.5	29.2
4	9	3	22.3	23.4
4	9	5	19.6	19.3
4	10	0	56.7	55.6
4	10	2	41.1	40.4
4	10	4	32.7	33.4
4	11	1	10.7	13.3
4	11	3	12.4	13.7
4	12	0	41.3	40.0
4	12	2	21.2	23.3
4	12	4	14.6	14.6
4	13	3	7.0	10.7
5	0	1	111.7	109.9
5	0	3	96.2	91.3
5	0	5	65.9	70.4
5	1	0	107.2	101.3
5	1	2	78.4	74.7
5	1	4	59.8	57.5
5	1	6	40.3	40.2
5	2	1	71.2	68.1
5	2	3	47.6	46.1
5	2	5	32.8	30.6
5	2	7	13.9	14.2
5	3	0	204.0	205.3
5	3	2	156.9	154.8
5	3	4	119.8	116.1
5	3	6	81.6	77.9
5	4	1	76.3	73.6
5	4	3	43.6	42.6
5	4	5	31.2	30.4
5	4	7	21.5	17.4
5	5	0	50.1	47.2
5	5	2	26.0	27.3
5	5	4	20.0	20.3
5	5	6	19.3	18.6
5	6	1	88.5	88.8
5	6	3	74.2	72.4
5	6	5	64.2	60.2
5	6	7	34.8	33.3
5	7	0	97.9	96.5
5	7	2	84.0	83.3
5	7	4	69.2	67.1
5	8	1	43.5	43.8
5	8	3	32.9	32.7
5	8	5	23.5	22.9
5	8	7	15.0	11.4
5	9	0	105.9	104.9
5	9	2	86.1	87.3
5	9	4	72.4	72.3
5	9	6	51.1	49.6
5	10	1	53.3	53.4
5	10	3	32.6	33.4
5	10	5	26.9	26.5
5	10	7	14.9	18.1
5	11	2	5.3	6.4
5	11	4	8.6	7.0
5	12	1	56.6	55.0
5	12	3	47.1	44.5
6	0	0	105.1	103.8
6	0	2	55.4	54.1
6	0	4	23.6	24.0
6	0	6	31.0	27.9
6	1	1	15.2	13.1
6	1	3	12.2	11.1
6	2	0	29.6	28.7
6	2	2	11.3	13.1
6	2	4	10.5	11.6
6	2	6	16.3	14.4
6	3	1	12.4	10.6
6	3	3	12.7	12.8
6	4	0	15.9	15.6
6	4	2	22.3	21.7
6	4	4	28.1	26.8
6	4	6	17.7	15.6
6	5	1	11.1	12.2
6	5	3	22.5	23.0
6	5	5	19.2	16.8
6	6	0	54.5	54.0
6	6	2	32.6	32.7
6	6	4	23.1	23.8
6	6	6	18.6	17.3
6	7	1	11.1	12.3
6	7	3	22.0	22.7
6	7	5	10.9	13.1
6	8	0	6.7	1.2
6	8	2	9.6	10.5
6	8	4	13.2	11.4
6	9	1	11.3	15.0
6	9	3	6.7	7.2
6	10	0	6.3	10.0
6	10	2	20.0	20.0
6	11	1	19.6	19.7
6	11	3	11.5	15.4
7	0	1	137.6	137.8
7	0	3	104.2	101.9
7	0	5	67.2	66.9
7	0	7	58.3	55.7
7	1	0	27.8	28.2
7	1	2	42.9	43.3
7	1	4	33.7	32.2
7	1	6	19.7	19.5
7	2	1	62.8	62.7
7	2	3	34.0	41.3
7	2	5	27.7	29.0
7	2	7	27.7	25.2
7	3	0	71.8	68.7
7	3	2	86.2	84.9
7	3	4	57.5	57.2
7	3	6	31.9	29.8
7	4	1	81.1	79.7
7	4	3	79.1	78.3
7	4	5	48.8	49.2
7	4	7	29.1	30.3
7	5	0	12.7	12.2
7	5	2	36.9	37.8
7	5	4	31.9	32.3
7	5	6	15.7	14.3
7	6	1	96.0	97.4
7	6	3	86.6	86.2
7	6	5	54.6	54.1
7	6	7	43.8	41.3
7	7	0	37.2	39.6
7	7	2	30.7	32.3
7	7	4	21.9	22.6
7	7	6	28.1	25.1
7	8	1	7.9	10.4
7	8	3	6.9	7.3
7	9	0	67.0	65.8
7	9	2	60.3	58.9
7	9	4	36.3	36.8
7	10	1	62.1	61.4
7	10	3	64.2	63.3
7	11	2	16.1	14.9
8	0	0	43.4	41.2
8	0	2	50.1	50.3
8	0	4	30.6	31.9
8	0	6	24.8	23.2
8	1	1	59.8	58.6
8	1	3	49.7	49.0
8	1	5	26.6	27.2
8	2	0	22.1	23.0
8	2	2	22.1	24.0
8	2	6	13.5	13.1
8	3	1	72.7	73.9
8	3	3	74.3	74.8
8	3	5	47.3	48.1
8	4	0	12.9	14.9
8	4	2	14.3	18.5
8	4	4	11.5	9.8
8	5	1	28.3	27.1
8	5	3	24.1	24.3
8	6	0	37.0	39.6
8	6	2	46.4	45.7
8	7	1	58.5	58.9
8	7	3	49.1	48.3
8	7	5	29.4	29.7
8	7	7	24.2	22.7
8	8	0	22.8	23.4
8	8	2	21.1	21.5
8	9	3	43.7	45.4
9	0	1	38.6	40.3
9	0	3	12.7	11.3
9	0	5	23.3	24.7
9	1	0	40.7	41.4
9	1	2	32.8	34.8
9	1	4	28.5	29.8
9	1	6	19.9	19.0
9	2	1	23.4	26.2
9	2	3	7.1	4.7
9	2	5	7.1	9.3
9	3	0	62.4	60.9
9	3	4	56.9	55.6
9	3	6	34.6	34.7
9	4	1	10.8	11.9
9	4	3	10.9	11.4
9	4	5	9.3	8.5
9	5	2	12.3	12.8
9	5	4	11.4	14.5
9	6	1	27.4	28.1
9	6	3	19.4	19.8
10	0	0	99.2	99.1
10	0	4	74.1	78.6
10	1	1	31.6	31.7
10	1	3	20.7	22.0
10	3	3	35.3	37.1
10	5	3	9.7	14.9
11	0	1	13.3	17.0
11	0	3	18.1	20.3

For the photographic data, where the $hk1$ and $hk\bar{1}$ layers were both included, the differences in the residuals were slightly greater. The final values of R were 7.51% and 7.12%, and of R' 0.0116 and 0.0107. Moreover, a detailed comparison of the observed and calculated $F(hkl)$ for the $hk1$ and $hk\bar{1}$ layers indicated that the agreement was clearly better for the polarity with the lower R value. Further support for this choice came from the Zn—O bond distances. For the preferred polarity these lengths showed a spread of only 0.034 Å, whereas for the reversed polarity the range was 0.107 Å. Relative to the polarity for the structure given by Barclay and Cox, the preferred polarity is the one for which our photographic data are in fact $hk\bar{7}$ to $hk1$, and our counter data are $hk\bar{7}$ to $hk0$.

Table 5. *Observed and calculated structure factors for the* $hk1$ *and* $hk\bar{1}$ *layers of the photographic data*

h	k	l	$F_o(-)$	$F_o(+)$	$F_c(-)$	$F_c(+)$	h	k	l	$F_o(-)$	$F_o(+)$	$F_c(-)$	$F_c(+)$	h	k	l	$F_o(-)$	$F_o(+)$	$F_c(-)$	$F_c(+)$
0	3	1	132.9	127.7	143.9	143.2	3	10	1	75.9	74.6	76.1	76.9	7	16	1	29.5	31.9	29.7	30.2
	5		49.3	47.8	51.2	48.6		12		48.4	49.2	49.4	49.9	8	1	1	54.9	55.5	51.9	51.8
	7		83.0	86.0	90.9	94.2		16		29.9	29.8	29.7	28.9		3		67.1	66.6	65.9	63.9
	9		86.9	88.3	97.0	100.1	4	1	1	13.2	15.3	12.0	14.4		5		22.1	22.1	23.9	23.4
	11		29.9	29.9	31.4	32.1		3		69.6	69.3	61.1	64.7		7		49.7	51.2	50.9	50.9
	13		44.2	44.1	43.8	44.3		5		31.2	31.0	28.1	29.5		9		36.2	37.5	38.0	36.2
	15		50.9	51.7	43.9	45.4		9		23.9	28.7	25.3	25.6		13		31.2	34.9	31.5	32.1
	19		20.2	19.4	22.0	21.3		15		16.2	15.5	16.3	16.9	9	0	1	32.8	36.0	34.4	37.4
1	4	1	27.5	29.1	29.2	31.7	5	0	1	110.2	107.5	104.7	104.9		2		23.4	24.2	21.8	23.5
	6		14.5	17.3	17.2	19.9		2		79.6	69.3	65.3	66.5		4		11.6	11.1	11.4	10.9
	8		25.6	24.6	26.5	26.9		4		75.5	75.2	70.8	72.4		6		23.2	26.9	23.7	24.9
	10		10.2	14.9	12.2	14.3		6		82.3	83.0	82.1	82.5		8		14.8	15.9	15.6	16.2
	12		18.8	20.2	18.5	20.0		8		39.4	41.2	38.3	38.9	10	1	1	30.2	29.1	27.6	28.6
	14		18.1	20.1	19.8	20.0		10		49.1	50.4	49.3	50.8		3		48.9	54.2	52.7	55.1
	16		11.5	11.1	5.8	5.8		12		49.6	54.2	47.9	48.9		5		30.0	32.8	28.1	29.6
2	1	1	181.9	182.0	145.5	145.2		14		17.7	17.0	16.9	17.3		7		21.5	19.3	21.2	19.0
	3		148.1	137.4	149.2	144.2		16		29.6	33.9	29.0	29.7		9		34.0	35.2	34.2	33.7
	5		55.6	52.5	53.8	52.5		18		20.3	27.6	22.7	23.4	11	0	1	14.8	14.3	14.1	14.3
	7		110.1	111.1	120.2	121.1	6	1	1	11.2	13.6	10.2	10.3	12	1	1	34.5	35.7	33.1	33.2
	9		78.0	72.0	82.3	80.8		3		7.3	8.6	9.8	10.1		3		56.1	56.5	53.4	53.4
	13		58.5	58.2	59.0	59.4		11		14.3	16.8	17.6	18.0		5		18.3	17.6	17.4	18.2
	15		26.0	26.1	26.7	25.7	7	0	1	123.7	121.8	127.0	127.7		7		35.8	36.3	32.7	31.6
	19		22.3	23.1	22.7	22.6		2		59.9	59.9	56.4	57.1		9		30.3	36.6	31.1	29.4
3	0	1	144.5	135.5	139.1	132.2		4		74.9	71.9	71.1	69.6	13	0	1	31.3	34.1	33.2	33.7
	2		76.0	73.6	71.6	67.5		6		87.8	86.0	87.5	86.3		4		12.1	8.2	17.0	16.0
	4		120.0	116.5	118.9	119.5		10		52.6	52.9	52.9	51.8		6		21.3	18.7	23.3	22.3
	6		105.9	105.5	110.4	108.9		12		35.5	35.7	36.8	34.5							
	8		14.3	10.4	15.9	13.0		14		11.8	8.0	13.4	13.5							

Table 2 gives the final atomic coordinates and e.s.d.'s from both sets of data together with the weighted means. The two independent sets of coordinates agree satisfactorily. The z coordinates of O(3), O(4) and O(5) differ by 0.25 to 0.43 Å from those given by Barclay and Cox.

Table 3 gives both sets of anisotropic vibration parameters. Here there are some significant differences, which are probably to be attributed to our neglect of absorption corrections for the two different crystals.

The observed and calculated structure factors for the diffractometer data are given in Table 4. The photographically observed pairs of structure factors $hk1$ and $hk\bar{1}$, together with the corresponding calculated values, are given in Table 5.

Discussion

General

The structure is best considered as a three-dimensional assembly of zinc-oxygen and silicon-oxygen tetrahedra, rather than as a structure made up of discrete Si_2O_7 groups. This is in accord with the scheme of classification proposed by ZOLTAI[12].

Figure 1 is a projection onto (010) of the contents of two half-cells bounded by $y = 0$ and $y = \frac{1}{2}$. This shows that the tetrahedra are linked in threes into rings of six atoms of which two are zinc, one silicon and three oxygen. These rings are linked in infinite sheets
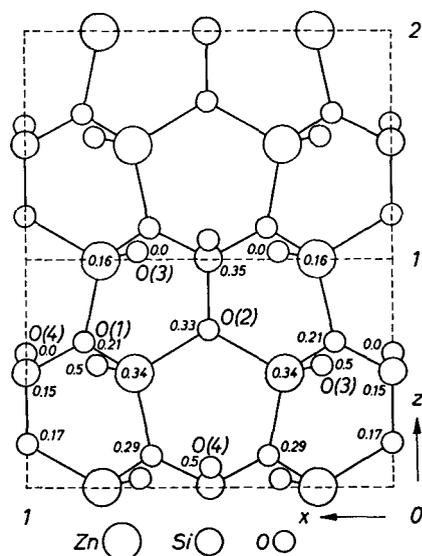
Fig. 1. (010) projection of the cell contents bounded by $y = 0$ and $y = \frac{1}{2}$

extending in the (010) planes. Each oxygen in such a sheet is linked to two zinc atoms and to one silicon. The fourth oxygen in each tetrahedron is involved in bridging between the sheets, Zn—O(3)—Zn and Si—O(4)—Si. These oxygens lie on the mirror planes at $y = 0$ and $y = \frac{1}{2}$. Thus in each tetrahedron three of the oxygens are three coordinate and one is two coordinate (so far as the network is concerned), giving a mean oxygen coordination of 2.75—the sharing coefficient in ZOLTAI's classification. The cross-linking of the sheets

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[12] TIBOR ZOLTAI, Classification of silicates and other minerals with tetrahedral structures. Amer. Min. **45** (1960) 960—973.

produces, in addition, rings of four, six and eight tetrahedra, as pointed out by ZOLTAI.

The linking of the sheets leaves large channels between the sheets. These may be seen in Fig. 2, which is a (001) projection and shows the linkage of the tetrahedra through shared corners. The channels along $\frac{1}{2}$, 0, z and 0, $\frac{1}{2}$, z open into large cavities at $z = 0$ and $z = \frac{1}{2}$, and the water molecules are situated close to the centres of these cavities. It is the connection of the cavities into channels in the z direction which permits the removal of the water on heating without disruption of the structure[13].
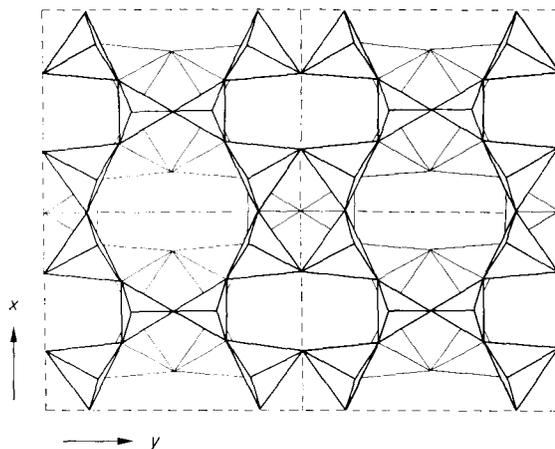
Fig. 2. (001) projection of four unit cells, showing the linking of the tetrahedra

The sheets of rings of six atoms are similar to those found in bertrandite[14], $Be_4Si_2O_7(OH_2)$, and in the iso-structural silicon oxy-nitride[15], Si_2ON_2. All three structures have the same cation to anion ratio of 2:3, and the same sharing coefficient of 2.75. In bertrandite and silicon oxynitride, however, the cross-linking of the sheets produces rings of only four and six tetrahedra, and as a result these structures do not have the channels found in hemimorphite.

[13] H. F. W. TAYLOR, The dehydration of hemimorphite. Amer. Min. 47 (1962) 932—944.

[14] L. P. SOLOV'EVA and N. V. BELOV, Precise determination of the structure of bertrandite $Be_4(Si_2O_7)(OH)_2$. Soviet Physics—Crystallography 9 (1964) 458—460.

[15] INGVAR IDRESTEDT and CYRILL BROSSET, Structure of Si_2N_2O. Acta Chem. Scand. 18 (1964) 1879—1886.

The zinc tetrahedron

The bond lengths and angles in the zinc tetrahedron are given in Table 6. The mean Zn—O length of 1.954 Å is about 0.02 Å shorter than the mean length of 1.973 Å found in the tetrahedral structure of zincite[16], ZnO (the latter value, calculated from the cell dimensions, is not appreciably dependent on the single positional parameter of the structure). The slight shortening may perhaps be associated with the fact that in hemimorphite the oxygens have trigonal coordination whereas in zincite their coordination is tetrahedral. In carbon compounds several authors[17] consider that there is a similar change in covalent radius with coordination number. The three angles between Zn—O(3) [the hydroxyl oxygen] and the other Zn—O bonds are slightly greater than tetrahedral (mean 111.9°), whilst the other three angles are slightly less than tetrahedral (mean 107.0°).

Table 6. *Interatomic distances and angles with their estimated standard deviations*

Zn—O(1)	1.959 ± 0.006 Å	Si—O(1)	1.626 ± 0.006 Å (2 ×)
Zn—O(1′)	1.947 ± 0.005 Å	Si—O(2)	1.631 ± 0.010 Å
Zn—O(2)	1.971 ± 0.004 Å	Si—O(4)	1.627 ± 0.004 Å
Zn—O(3)	1.941 ± 0.004 Å		
O(1)—O(1′)	3.117 ± 0.008 Å	O(1)—Zn—O(1′)	105.9 ± 0.2°
O(1)—O(2)	3.159 ± 0.010 Å	O(1)—Zn—O(2)	107.0 ± 0.3°
O(1)—O(3)	3.267 ± 0.011 Å	O(1)—Zn—O(3)	113.8 ± 0.5°
O(1′)—O(2)	3.168 ± 0.006 Å	O(1′)—Zn—O(2)	108.0 ± 0.3°
O(1′)—O(3)	3.190 ± 0.006 Å	O(1′)—Zn—O(3)	110.3 ± 0.3°
O(2)—O(3)	3.235 ± 0.009 Å	O(2)—Zn—O(3)	111.6 ± 0.4°
O(1)—O(1′)	2.659 ± 0.007 Å	O(1)—Si—O(1′)	109.7 ± 0.4°
O(1)—O(2)	2.681 ± 0.009 Å (2 ×)	O(1)—Si—O(2)	110.8 ± 0.3° (2 ×)
O(1)—O(4)	2.603 ± 0.005 Å (2 ×)	O(1)—Si—O(4)	106.4 ± 0.4° (2 ×)
O(2)—O(4)	2.709 ± 0.013 Å	O(2)—Si—O(4)	112.5 ± 0.6°
Zn—O(3)—Zn′	125.8 ± 0.5°	Si—O(4)—Si′	150.3 ± 0.9°
O(5)—O(3)	2.890 ± 0.041 Å (2 ×)	O(3)—O(5)—O(3)	67.7 ± 0.9°
O(5)—O(3′)	3.160 ± 0.043 Å (2 ×)	O(3′)—O(5)—O(3′)	61.2 ± 0.9°
Zn—O(1)—Si	116.7 ± 0.4°	Zn—O(2)—Si	119.1 ± 0.2° (2 ×)
Zn′—O(1)—Si	128.4 ± 0.4°	Zn—O(2)—Zn′	120.5 ± 0.4°
Zn—O(1)—Zn′	114.3 ± 0.3°		

[16] H. E. Swanson and R. K. Fuyat, Standard x-ray diffraction powder patterns. National Bureau of Standards circular 539, Vol. II (1953) 25—26.

[17] David R. Lide, Jr., A survey of carbon-carbon bond lengths. Tetrahedron 17 (1962) 125—134.

The Si_2O_7 group

The Si_2O_7 group has crystallographic symmetry $mm2$; its detailed dimensions are given in Table 6. The unusual bridge bond-length found by Barclay and Cox is not confirmed. The revised distance of 1.627 ± 0.004 Å is not significantly different from the terminal Si—O distances of 1.631 ± 0.010 Å and 1.626 ± 0.006 Å. The bridging Si—O—Si angle of $150.3 \pm 0.9°$ is a fairly typical value.

A consideration of the π bonding in an isolated $Si_2O_7{}^{6-}$ ion leads to the prediction[4] that the terminal bonds should be shorter than the bridge bonds. However there is clearly some covalent character in the Zn—O bonds (41% on Pauling's arguments[18] as compared with 49% for Si—O). The assumption of an isolated $Si_2O_7{}^{6-}$ ion is therefore invalid, and on the terminal oxygens the lone pairs of electrons, which are used in π bonding to the silicon, will also be involved in bonding to zinc. The covalent aspect of the Zn—O bonds is consistent with the observed bond angles at oxygen atoms O(1) and O(2), given in Table 6. Each of these atoms is linked to two zinc atoms and to one silicon, and the angles at oxygen are close to $120°$, suggesting sp^2 hybridization. If the Zn—O and Si—O σ bonds were of equal strength, this would leave only one lone pair on the terminal oxygens available for π bonding instead of two, and relatively long terminal bonds would be expected in the disilicate group. The actual equality of the Si—O bond lengths, as contrasted with the irregularities expected for an isolated disilicate ion, is consistent with the description of the structure as a three-dimensional network of zinc-oxygen and silicon-oxygen tetrahedra. Zoltai's classification is therefore more realistic than the older descriptions in terms of isolated Si_2O_7 groups.

The water molecule

The water molecule occupies a special position of $mm2$ symmetry at the centre of a cavity formed by 20 oxygen atoms of the tetrahedral framework. Fig. 3 shows the $y = 0$ section through the centre of one of these cavities. The oxygen atoms on the mirror plane at $y = 0$ are shown together with the zinc atoms lying above and below the plane. A final difference map gave no clear indication of either the hydroxyl or water hydrogen positions. It seems probable that the O(5)—O(3) distances of 2.89 Å represent weak hydrogen bonds, but the

[18] Linus Pauling, The nature of the chemical bond. 3rd Ed., Cornell University Press, 1960, 97—102.

O(3)—O(5)—O(3) angle of 68° requires that the hydrogens be considerably displaced from the O(5)—O(3) lines. The very high e.s.d. (0.05 Å) of the z coordinate of the water oxygen and its high vibration parameters normal to this direction suggest that it may be rather free to move inside the cavity and to form weak hydrogen bonds to any of the twenty neighbouring oxygens.
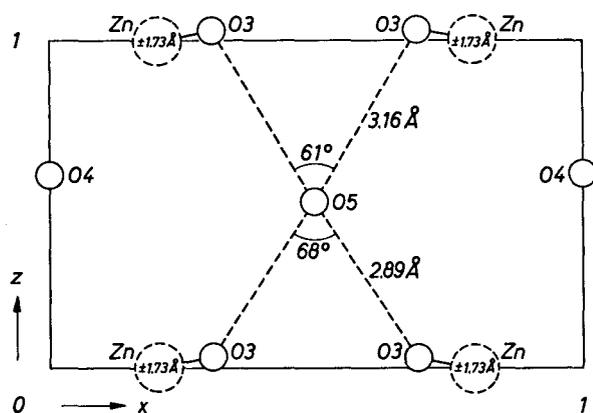
Fig. 3. Section at $y = 0$, showing the environment of the water molecule

Acknowledgements