CHU, S. S. C. & JEFFREY, G. A. (1967). *Acta Cryst.* **23**, 1038.
CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* **24**, 830.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
ELIEL, E. L., ALLINGER, N. L., ANGYAL, S. J. & MORRISON, G. A. (1966). *Conformational Analysis*. New York: John Wiley.
GATEHOUSE, B. M. & POPPLETON, B. J. (1970). *Acta Cryst.* B**26**, 1761.
GROSS, D. (1962). *Methods in Carbohydrate Chemistry*, Vol. 1, p. 360. Edited by R. L. WHISTLER, M. L. WOLFROM, J. N. BEMILLER & F. SHAFIZADEH. New York & London: Academic Press.
HALL, S. R. (1968). *Direct Phasing Methods Program, UWAC-17*. Univ. of Western Australia. Revised for IBM 7090 by H. M. BERMAN.
HOUGH, L. & RICHARDSON, A. C. (1967). *Rodd's Chemistry of Carbon Compounds*, Vol. 1F, Ch. 23. Edited by S. COFFEY. New York: Elsevier.

JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
KARLE, J. & HAUPTMAN, M. (1956). *Acta Cryst.* **9**, 635.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
KIM, S. H. & ROSENSTEIN, R. D. (1967) *Acta Cryst.* **22**, 648.
KLYNE, W. & PRELOG, V. (1960). *Experienta*, **16**, 521.
ROHRER, D. (1972). *Acta Cryst.* In the press.
SHIONO, R. (1968). Unpublished work.
SHIONO, R. (1969). Unpublished work.
STANĚK, J., ČERNÝ, M. & PACÁK, J. (1965). *The Oligosaccharides*, p. 258. New York and London: Academic Press.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
SUNDARALINGAM, M. (1965). *J. Amer. Chem. Soc.* **87**, 599.
SUNDARALINGAM, M. (1970). Private communication.
TIPSON, R. (1970). Private communication.

Synthetic Magnesian Merrihueite, Dipotassium Pentamagnesium Dodecasilicate: a Tetrahedral Magnesiosilicate Framework Crystal Structure

BY AIJAZ A. KHAN, WERNER H. BAUR AND WARREN C. FORBES

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

The compound $K_2Mg_5Si_{12}O_{30}$ was synthesized hydrothermally at 790°C and 2000 bars P_{H_2O}, its composition verified by electron microscope analysis and its crystal structure determined. $K_2Mg_5Si_{12}O_{30}$ is isostructural with milarite: space group $P6/m$ $2/c$ $2/c$, $a = 10\cdot222$ (2), $c = 14\cdot152$ (2) Å, $Z = 2$. Single-crystal diffractometer data were refined to $R = 0\cdot028$ for 528 F_{obs}. This phase has the structural formula $Mg_2^{[6]}K^{[9]}K^{[12]}Mg_3^{[4]}Si_{12}^{[4]}O_{30}$, where the coordination number is indicated in brackets. The SiO_4 tetrahedra form hexagonal double rings with the composition $Si_{12}O_{30}$. These double rings are linked by magnesium atoms in tetrahedral four-coordination to form a tetrahedral magnesiosilicate framework structure, the first to be described. One half of the K atoms are located in 9-coordinated sites ($\frac{1}{3},\frac{2}{3},0$ *etc.*) which have not been found to be populated in other milarite-group structures. On the basis of this structure determination, we propose $A_2^{[6]}B_2^{[9]}C^{[12]}D^{[18]}T2_3^{[4]}T1_{12}^{[4]}O_{30}$ as a general crystal-chemical formula for milarite-type structures.

Introduction

The compound $K_2Mg_5Si_{12}O_{30}$ was first synthesized by Roedder (1951) while he was studying the phase relations of the system $K_2O-MgO-SiO_2$. Olsen (1967) analyzed Roedder's material using a microprobe and thus confirmed the composition. Seifert & Schreyer (1969) synthesized the compound under both hydrothermal and dry conditions and determined the lattice constants. These studies established that the compound is isostructural with milarite, $KCa_2Be_2Al(Si_{12}O_{30})\cdot\frac{1}{2}H_2O$ (Ito, Morimoto & Sadanaga, 1952) and osumilite, $(K,Na)(Fe,Mg)_2(Al,Fe)_3(Al,Si)_{12}O_{30}$ (Miyashiro, 1956). Because of the analogy in the chemical formulas it appears that three Mg atoms per formula unit in $K_2Mg_2(Mg_3Si_{12}O_{30})$ should be in tetrahedral 4-coordination. Such coordination is very rare; the only reported case of a silicate with Mg in 4-coordination is

melilite $(Ca,Na)_2(Mg,Al)Si_2O_7$ (Smith, 1953), where Mg and Al atoms are statistically distributed over one site. Furthermore $K_2Mg_5Si_{12}O_{30}$ contains twice as much potassium as can be accommodated in the K-sites known from the milarite structure. In order to verify the occurrence of magnesium in 4-coordination and to find out which sites are occupied by the excess potassium atoms the crystal structure of $K_2Mg_5Si_{12}O_{30}$ was determined.

Experimental

The compound $K_2Mg_5Si_{12}O_{30}$ was produced by the decomposition of a synthetic mica, $KMg_3Si_4O_{11}(OH)$, at 790°C and 2000 bars P_{H_2O} (Forbes, 1972). The composition was verified by electron microprobe analysis: $K_2O = 9\cdot38$, $MgO = 19\cdot69$, $SiO_2 = 70\cdot82$ weight per cent, as compared with the values of 9·26, 19·82 and 70·91 weight per cent calculated for the ideal composition.

The analysis total of 99·89 per cent precludes the presence of any additional components, such as H_2O. Additional hydrothermal experiments, using a stoichiometric $K_2O.5MgO.12SiO_2$ mixture showed that the synthesis products are strongly influenced by the nature of the starting materials. Using an oxide starting material, the 1:5:12 phase could be synthesized only in a restricted P–T range (*e.g.* 750–840°C at 1000 bars P_{H_2O}). At temperatures below 750°C, a $KMg_{2\cdot5}Si_4O_{10}(OH)_2$–quartz–vapor assemblage was produced. Above 840°C, a clinoenstatite–glass–vapor was found. However, use of a forsterite–glass starting material showed the synthesis field of $K_2O.5MgO.12SiO_2$ to be comparable to the stability field reported by Seifert & Schreyer (1969).

The crystal used for data collection was of approximately isometric shape with an average diameter of 0·028 cm. Crystal data are: F.W. 1016·8; hexagonal, space group $P6/m\ 2/c\ 2/c$, from absences (hhl and $h\bar{h}l$ both present with $l=2n$ only) and the successful refinement of the crystal structure; $a=10\cdot222$ (2), $c=14\cdot152$ (2) Å, $V=1280\cdot6$ Å^3, $D_x=2\cdot636$ g.cm^{-3}, $Z=2$, $\mu(\text{Ag } K\alpha)=6\cdot1$ cm^{-1}, $\mu R=0\cdot09$. Intensity data were collected on a computer-controlled diffractometer [$\lambda(\text{Ag } K\bar{\alpha})=0\cdot56083$ Å]. For details of the experimental procedures see Baur & Khan (1970), except that graphite-crystal monochromated radiation has been used. All possible reflections in a sphere of radius $\sin\theta/\lambda=0\cdot75$ Å^{-1} were collected. The total of 9871 measured intensities was reduced to a set of 975 unique reflections of which 447 were zero or smaller than two times their standard deviation in which case they were considered to be zero. In view of the regular shape of the crystal and of the small μR-value the absorption correction was negligible.

The positional parameters of osumilite (Miyashiro, 1956) were used as starting parameters for the refinement. A difference synthesis revealed that the excess potassium is located in equipoint 4(d) at $\frac{1}{3},\frac{2}{3},0$ *etc.* Since these sites have fourfold multiplicity and only two potassium atoms per unit cell have to be placed, the occupancy factor for these sites is 0·5. A refinement of the site-occupancy factors of both K(1) and K(2) resulted in values of 0·992 and 0·475 respectively, in reasonable agreement with the ideal values. The refinement with anisotropic temperature factors resulted in $R=0\cdot028$ and $Rw=0\cdot035$ for 528 observed F_{hkl}. The final difference synthesis showed no peaks higher than 0·5 e.Å^{-3} (in the vicinity of the Si site). The $|F_o|$, $|F_c|$ and σ's are shown in Table 1, the final positional and thermal parameters in Table 2.

Discussion of the crystal structure

The crystal-chemical formula of this compound can be written as $\mathrm{Mg}_2^{[6]}\mathrm{K}^{[9]}\mathrm{K}^{[12]}\mathrm{Mg}_3^{[4]}\mathrm{Si}_{12}^{[4]}\mathrm{O}_{30}$, where the coordination numbers are indicated as superscripts in square brackets. The main features of the crystal structure of $K_2Mg_5Si_{12}O_{30}$ (see Fig. 1) are the same as described by the previous investigators for milarite and osumilite. The coordination tetrahedra around the silicon atoms in position $T1$ (for an explanation of the site-nomenclature see Table 3) form hexagonal double rings of composition $Si_{12}O_{30}$, centered around equivalent positions 2(b), (0,0,0 and 0,0,$\frac{1}{2}$). The O(2) oxygen atoms link the tetrahedra within the rings, while the O(1) atoms connect the rings with each other, thus forming the double hexagonal rings. The oxygen atoms O(3) are terminal at the silicon coordination tetrahedra, but since they are also coordinated to Mg(2) in $T2$,

Table 1. $K_2Mg_5Si_{12}O_{30}$, *observed and calculated structure factors* (×2) *and σ's* (×10) *used in the least-squares procedure*

L	FO	FC	SIG
H=	0,	K=	0
2	213	200	19
4	437	449	40
6	164	156	16
8	596	644	55
10	48	52	15
12	96	93	15
14	244	248	25
16	199	201	22
18	176	170	21
20	74	63	22
H=	1,	K=	0
2	35	28	6
4	150	141	14
6	70	67	10
8	77	76	11
12	91	93	15
14	23	24	34
H=	1,	K=	1
0	179	170	16
2	136	126	13
4	342	340	31
6	15	11	22
8	97	95	12
10	101	102	14
12	138	138	17
14	25	25	32
18	63	63	22
H=	2,	K=	0
0	262	258	24
2	252	240	23
4	316	312	29
6	121	121	13
8	129	127	14
10	164	167	18
12	120	120	16
18	98	97	19
H=	2,	K=	1
0	74	65	8
1	276	267	25
2	46	42	8
3	136	128	13
4	28	30	12
7	80	78	12
9	98	100	14
10	85	88	14
11	170	174	15
13	74	77	16
14	55	56	19
15	61	62	15
17	113	115	19
18	62	63	24
19	66	63	23
H=	2,	K=	2
0	381	389	35
2	23	29	12
4	140	139	14
6	280	285	26
8	373	395	35
10	27	28	25
12	27	28	28
14	125	123	18
16	129	128	19
20	94	83	21
H=	3,	K=	0
0	120	116	12
2	19	16	16
4	121	115	13
6	92	90	12
8	159	162	17
10	19	8	29
16	50	50	22
20	43	42	31
H=	3,	K=	1
0	159	154	15
1	104	104	11
2	43	43	10
3	167	161	16
4	183	179	18
5	201	204	20
6	36	39	14
7	36	33	15
8	20	15	25
9	284	297	27
11	54	56	17
12	43	41	19
13	156	157	15
15	34	33	27
17	108	109	19
19	88	88	21
H=	3,	K=	2
0	137	136	14
1	19	19	19
2	71	69	10
3	34	36	13
5	19	18	23
6	27	26	19
7	27	28	21
8	117	121	15
10	64	66	15
11	55	61	16
13	37	35	22
15	52	52	21
16	39	38	26
17	48	47	24
18	36	39	32
H=	3,	K=	3
0	215	215	21
2	39	38	14
4	292	298	28
6	37	39	16
8	60	59	14
10	88	91	16
12	94	94	16
14	66	66	18
18	88	86	21
H=	4,	K=	0
0	31	29	12
2	194	192	19
4	55	54	11
6	70	68	12
9	32	33	19
10	188	196	20
12	35	35	22
14	26	29	32
18	120	119	20
H=	4,	K=	1
0	163	157	16
1	171	169	17
2	72	72	11
3	60	59	11
4	114	113	13
5	62	61	12
6	58	57	13
7	114	115	14
8	36	38	20
9	93	95	15
10	67	67	15
11	22	23	32
12	98	97	16
15	31	31	31
16	31	32	33
H=	4,	K=	2
0	138	138	13
1	65	64	11
2	55	59	12
3	43	44	13
4	86	85	13
5	83	82	13
6	132	134	14
8	89	92	14
9	68	72	15
12	41	40	21
13	52	53	19
14	56	65	18
16	41	41	27
17	27	30	40
H=	4,	K=	3
0	26	26	21
1	94	95	13
2	20	22	27
3	23	24	24
4	23	22	25
5	122	125	15
6	21	22	28
7	52	55	16
8	57	59	16
9	155	157	18
11	35	37	24
13	45	46	23
15	36	37	28
H=	4,	K=	4
0	25	21	22
2	104	105	14
4	255	264	25
6	117	119	16
8	72	70	16
10	115	120	17
12	98	96	17
16	50	46	25
18	104	98	21
H=	5,	K=	0
0	185	190	19
2	20	22	20
4	59	58	12
6	31	34	18
8	50	49	15
10	25	24	28
14	51	48	20
16	27	22	37
18	43	44	30
H=	5,	K=	1
1	204	205	20
2	77	77	12
3	97	99	13
4	62	63	13
5	146	149	16
6	81	82	14
7	69	71	14
8	65	65	15
9	172	177	19
10	98	95	16
11	34	34	23
12	66	67	18
13	112	113	17
14	43	45	24
15	40	37	25
17	97	98	20
18	52	50	26
19	67	63	23
H=	5,	K=	2
0	341	358	32
1	144	145	16
3	85	86	13
4	103	105	14
5	45	45	16
6	68	67	14
7	90	92	15
8	219	225	23
9	63	65	16
10	89	90	16
14	104	103	19
16	76	75	20
17	33	34	35
18	89	86	21
H=	5,	K=	3
0	32	31	20
1	164	169	18
3	174	180	19
4	83	83	14
5	120	122	16
7	84	87	16
9	76	77	16
12	35	34	26
13	75	75	19
15	31	30	35
17	56	55	25
H=	5,	K=	4
0	64	56	15
1	86	86	15
3	31	34	23
4	28	30	24
5	27	25	26
6	24	20	27
7	26	26	28
8	66	67	17
9	58	57	18
11	49	48	22
13	36	36	28
15	31	29	36
17	61	58	24
H=	5,	K=	5
0	33	37	24
2	43	45	15
4	75	75	16
12	67	66	15
H=	6,	K=	0
0	181	185	19
2	216	223	22
4	205	213	21
6	20	19	28
10	116	114	16
12	193	197	22
14	111	110	18
16	47	46	25
H=	6,	K=	1
0	117	118	15
1	32	34	19
3	27	32	23
5	28	29	22
6	41	41	18
8	38	38	21
9	24	24	30
10	27	15	33
12	43	40	22
13	26	26	35
H=	6	K=	2
0	92	95	14
1	76	78	14
2	124	126	16
3	60	62	15
5	78	79	15
6	27	26	25
7	22	25	31
8	35	33	23
9	70	69	16
10	121	122	17
12	26	24	33
13	60	58	20
17	43	40	28
H=	6,	K=	3
0	87	88	15
1	82	83	15
3	29	31	23
4	65	66	15
5	54	53	17
7	27	29	28
8	102	103	17
9	76	75	17
12	28	26	32
13	42	41	26
16	42	41	30
17	46	44	30
H=	6,	K=	4
0	90	91	16
1	108	111	16
3	75	78	16
5	125	128	18
6	114	115	17
7	25	28	31
8	93	95	17
9	116	117	19
10	29	29	32
13	97	95	20
14	84	82	21
15	37	34	33
16	36	35	36
H=	6,	K=	5
0	90	90	17
1	22	15	30
5	25	24	32
8	31	32	31
9	28	29	34
10	45	45	25
14	46	44	20
H=	6,	K=	6
0	164	164	20
2	97	97	18
4	85	85	18
6	64	63	20
8	50	48	23
10	113	111	20
12	125	118	20
H=	7,	K=	0
0	219	227	22
4	140	144	17
8	104	104	16
10	40	42	22
12	27	28	32
14	66	66	20
16	27	28	41
18	58	55	26
H=	7,	K=	1
1	30	32	22
2	28	23	23
3	26	30	25
4	132	134	17
7	34	36	23
10	59	59	18
11	24	26	36
12	73	70	18
14	46	44	25
H=	7,	K=	2
0	98	97	15
1	67	70	16
2	49	49	17
3	106	108	16
4	35	35	22
6	61	61	18
7	54	57	18
8	93	93	17
9	31	31	28
10	97	97	17
14	64	62	21
16	33	33	27
H=	7,	K=	3
0	54	54	18
1	32	32	23
4	62	61	17
5	51	51	19
10	43	44	24
11	55	53	22
14	40	43	31
15	29	23	39
H=	7,	K=	4
0	132	133	18
1	64	64	18
5	73	74	18
6	46	47	21
8	75	77	20
9	93	92	19
10	44	43	26
13	48	46	27
14	82	79	22
H=	7,	K=	5
0	64	63	19
3	34	35	28
8	31	29	32
10	30	31	37
H=	7	K=	6
0	68	66	19
1	57	56	21
4	81	80	20
5	54	54	23
6	30	32	35
8	64	63	22
9	70	68	21
10	32	30	35
H=	7,	K=	7
0	100	97	20
4	38	37	32
6	57	59	25
8	91	86	21
H=	8,	K=	0
0	249	258	25
4	56	56	16
6	82	82	16
8	144	147	18
10	79	82	18
14	131	130	20
16	61	61	24
H=	8,	K=	1
0	33	34	22
1	22	24	32
2	19	5	29
4	77	78	16
5	60	60	17
6	28	28	28
7	23	20	32
9	59	61	19
10	34	33	28
11	37	37	27
12	39	37	28
14	43	41	28
H=	8,	K=	2
2	76	76	16
4	192	194	21
6	64	65	18
8	49	48	21
10	101	101	18
12	80	79	20
H=	8,	K=	3
1	69	71	18
3	44	44	21
4	31	31	28
5	104	104	18
9	97	96	19
10	29	27	35
13	75	71	21
14	30	31	42
H=	8,	K=	4
0	25	20	33
1	52	51	21
2	52	51	21
3	29	30	32
4	56	56	21
5	67	67	20
6	56	54	21
9	66	65	21
10	30	34	39
12	28	25	41
H=	8,	K=	5
0	25	22	35
1	30	27	33
3	30	26	32
4	100	99	19
5	29	26	34
H=	8,	K=	6
0	33	34	33
1	53	51	24
2	48	49	26
3	42	38	26
5	56	54	24
6	28	29	40
H=	8,	K=	7
0	57	54	24
4	41	39	30
H=	9,	K=	0
0	197	197	22
2	22	24	33
4	81	82	17
6	135	134	18
8	175	177	21
10	110	108	18
12	49	49	25
14	119	118	21
H=	9,	K=	1
0	55	57	19
2	25	25	30
3	25	23	31
4	25	5	21
6	27	23	31
8	62	64	20
10	34	33	31
11	33	33	33
H=	9,	K=	2
0	27	24	31
3	30	32	29
6	40	39	25
8	29	31	35
9	53	49	22
10	36	35	30
11	30	28	36
12	26	19	38
H=	9,	K=	3
0	60	60	20
1	70	70	19
3	28	29	34
5	62	62	21
6	32	33	31
7	27	26	37
8	70	69	21
9	76	74	21
H=	9,	K=	4
0	45	43	24
4	30	32	35
5	42	41	28
6	25	21	39
8	53	49	24
9	28	28	41
H=	9,	K=	5
0	36	34	33
1	42	42	29
5	57	56	24
H=	9,	K=	6
4	67	62	23
H=	10,	K=	0
0	67	66	18
2	55	53	19
4	97	97	18
6	48	46	22
10	68	66	20
12	30	30	39
H=	10,	K=	1
0	42	46	25
1	65	65	19
3	48	45	21
4	79	78	18
6	45	43	24
7	52	50	23
10	36	37	31
12	72	72	23
H=	10,	K=	2
0	111	109	19
1	39	38	25
2	30	27	30
4	52	52	22
5	52	51	23
6	60	60	22
8	94	91	20
9	51	50	26
H=	10,	K=	3
0	32	29	32
1	98	98	20
3	107	103	19
4	55	52	23
5	63	61	22
7	54	51	25
9	36	38	35
H=	10,	K=	4
0	66	64	22
1	39	39	31
3	28	26	39
4	71	68	21
5	51	49	26
6	54	52	26
H=	10,	K=	5
0	81	81	22
1	52	47	26
H=	11,	K=	0
0	68	65	20
4	26	27	38
H=	11,	K=	1
1	93	91	19
3	47	45	24
4	57	54	22
5	100	99	20
6	38	39	30
7	33	33	34
8	30	29	37
9	111	106	20
10	32	32	37
H=	11,	K=	2
0	70	67	20
8	47	45	28
H=	11,	K=	3
0	79	73	20
4	31	33	37
H=	12,	K=	0
0	104	104	20
2	72	66	15
4	54	53	23
8	30	27	38
H=	12,	K=	1
0	41	38	30
1	33	33	35
3	33	33	35
5	66	62	22
H=	12,	K=	2
2	33	30	36
H=	13,	K=	0
0	71	70	24
4	40	41	33

the other tetrahedrally four-coordinated cation, one can view the tetrahedra around $T1$ and $T2$ as forming a tetrahedral framework structure (Zoltai, 1960). Aluminosilicate frameworks have been encountered in many silicate minerals, however this is the first documented case of a magnesiosilicate tetrahedral framework. The remaining two Mg atoms per formula unit are located in the octahedrally coordinated A sites, $4(c)$, the sites which are occupied by Ca atoms in milarite. The potassium atoms are distributed over two locations: the twelve-coordinated C sites [$2(a)$, as in milarite] and the B sites, $4(d)$, which previously have not been reported as being populated in milarite-type structures. The coordination number of the B sites is nine with three short $K(2)-O(1)$ distances and six longer bonds to $O(3)$. The coordination polyhedron resembles a truncated trigonal dipyramid.

Seifert & Schreyer (1969) have observed that the values of the cell constants of $K_2Mg_5Si_{12}O_{30}$ ($a = 10\cdot22$ $c = 14\cdot15$ Å) differ substantially from those of $Na_2Mg_5Si_{12}O_{30}$, or merrihueite, $(K, Na, Ca)_2Fe_2(Fe, Mg)_3Si_{12}O_{30}$, and of roedderite, $(Na, K)_2Mg_2(Mg, Fe)_3Si_{12}O_{30}$, which all have an $a = 10\cdot15 \pm 0\cdot01$ and $c = 14\cdot29 \pm 0\cdot03$ Å. Osumilite with $a = 10\cdot16$ and $c = 14\cdot28$ Å may be added to this second list. The difference in the cell constants between $K_2Mg_5Si_{12}O_{30}$ and osumilite can be explained by the occupation of the B sites by potassium atoms. In order to accommodate the large K atoms the $O(1)$ oxygen atoms are pushed aside, thus increasing the value of the a cell constant. At the same time the $O(3)$ atoms are closer to the $K(2)$ atoms of the B sites in $K_2Mg_5Si_{12}O_{30}$, than they are in osumilite, where the B sites are vacant, thus reducing the length of the c cell constant. This is borne out by the distances and angles involving B,

$O(1)$ and $O(3)$. In osumilite (Brown & Gibbs, 1969) the distance $B-O(1)$ equals 2·45 Å, $B-O(3)$ equals 3·18 Å [compare with Table 4(a)]. The angle $O(3)-O(1)-O(3)$ is 145°, the distance $O(3)-O(3)$ is 5·11 Å in osumilite; the corresponding values in $K_2Mg_5Si_{12}O_{30}$ are 133° and 4·82 Å. Thus the presence of the large K ion in the B sites *increases* the a cell constant by about 0·07 Å, and *decreases* the c cell constant by approximately 0·14 Å. In $Na_2Mg_5Si_{12}O_{30}$, in merrihueite (the only analyzed sample of merrihueite contains an approximately equal number of K and Na atoms; Dodd, van Schmus & Marvin, 1965) and in roedderite the B sites have to be occupied, but they can be populated by Na atoms, which would easily fit into the dimensions of the void as it exists in osumilite. Therefore comparatively large a and small c cell constants in this type of structure can be taken as an indication of the presence of large atoms in the B sites. Of course such a comparison can only be made for chemically similar members of the milarite mineral group, as has been done here. Milarite itself, which has ions of very different sizes in both the A and $T2$ sites, cannot be compared with $K_2Mg_5Si_{12}O_{30}$ in this way.

There are two additional sites (D and E) which possibly may be occupied in milarite-type structures. There is no evidence that the 18-coordinated D sites inside of the hexagonal double ring are occupied in $K_2Mg_5Si_{12}O_{30}$. Ito *et al.* (1952) assumed that a water molecule is located in one half of the D sites in milarite, thus giving them an occupancy factor of 0·5. But their work is not of sufficiently high precision to establish this beyond doubt. Moreover Pasheva & Tarkhova (1953) in their refinement of the milarite structure did not confirm the presence of this water molecule. Brown & Gibbs (1969) had originally assumed that

Table 2. $K_2Mg_5Si_{12}O_{30}$, *positional and thermal parameters* ($\times 10^4$) *with their standard deviations*

The x, y, z are in fractions of the cell edge ($\times 10^4$). The definition of the temperature factor is

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	Equipoint	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	$2(a)$	0	0	2500	32 (2)	32	23 (2)	16	0	0
K(2)	$4(d)$	3333	6667	0	28 (2)	28	18 (2)	14	0	0
Mg(1)	$4(c)$	3333	6667	2500	16 (2)	16	14 (2)	8	0	0
Mg(2)	$6(f)$	5000	0	2500	30 (3)	20 (3)	12 (1)	10	0	0
Si	$24(m)$	1126 (1)	3484 (1)	1124 (1)	21 (1)	29 (1)	8 (1)	13 (1)	−1 (1)	−2 (1)
O(1)	$12(l)$	1239 (4)	3788 (4)	0	62 (4)	62 (4)	9 (1)	32 (4)	0	0
O(2)	$24(m)$	2183 (3)	2763 (3)	1396 (2)	50 (3)	55 (3)	17 (1)	39 (3)	1 (2)	3 (2)
O(3)	$24(m)$	1551 (3)	4968 (3)	1708 (2)	32 (2)	29 (2)	14 (1)	15 (2)	−1 (2)	0 (2)

Table 3. *Possible cation and/or water sites in milarite-type structures*

Symbol	Equipoint	Coordination number	Site symmetry	Coordinates x, y, z		
$T1$	$24(m)$	4	1	0·11	0·35	0·11
$T2$	$6(f)$	4	222	$\frac{1}{2}$	0	$\frac{1}{4}$
A	$4(c)$	6	32	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
B	$4(d)$	9 ($= 3 + 6$)	$\bar{6}$	$\frac{1}{3}$	$\frac{2}{3}$	0
C	$2(a)$	12	62	0	0	$\frac{1}{4}$
D	$2(b)$	18 ($= 12 + 6$)	$6/m$	0	0	0
E	$6(g)$	12 ($= 2 + 10$)	$2/m$	$\frac{1}{2}$	0	0

Table 4. $K_2Mg_5Si_{12}O_{30}$, *interatomic distances and bond angles*

a) Coordinations around K

K(1)—O(2)	(12×)	3·015 (2) Å
K(2)—O(1)	(3×)	2·635 (3)
K(2)—O(3)	(6×)	3·003 (2)

(b) Octahedron around Mg(1)

Mg(1)-O(3)	(6×)	2·104 (2) Å
O(3)—O(3)	(3×)	2·784 (3)
O(3)—O(3)	(3×)	2·943 (3)
O(3)—O(3)	(3×)	4·206 (4)
O(3)—O(3)	(6×)	3·085 (3)
O(3)—Mg(1)-O(3)	(3×)	82·8 (1)°
O(3)—Mg(1)-O(3)	(3×)	88·7 (1)
O(3)—Mg(1)-O(3)	(3×)	176·0 (1)
O(3)—Mg(1)-O(3)	(6×)	94·3 (1)

(c) Tetrahedron around Mg(2)

Mg(2)-O(3)	(4×)	1·955 (2) Å
O(3)—O(3)	(2×)	2·784 (3)
O(3)—O(3)	(2×)	3·204 (3)
O(3)—O(3)	(2×)	3·544 (3)
O(3)—Mg(2)-O(3)	(2×)	90·8 (1)°
O(3)—Mg(2)-O(3)	(2×)	110·1 (1)
O(3)—Mg(2)-O(3)	(2×)	130·0 (1)

(d) Tetrahedron around Si

Si——O(1)		1·613 (1) Å
Si——O(2)		1·625 (2)
Si——O(2)		1·630 (2)
Si——O(3)		1·585 (2)
O(1)—O(2)		2·646 (3)
O(1)—O(2)		2·635 (3)
O(1)—O(3)		2·649 (3)
O(2)—O(2)		2·579 (3)
O(2)—O(3)		2·616 (3)
O(2)—O(3)		2·673 (3)
O(1)—Si——O(2)		109·6 (1)°
O(1)—Si——O(2)		108·7 (1)
O(1)—Si——O(3)		111·8 (1)
O(2)—Si——O(2)		104·8 (1)
O(2)—Si——O(3)		109·2 (1)
O(2)—Si——O(3)		112·5 (1)

(e) Other distances

K(1)——Si	(12×)	3·702 (1) Å
K(2)——Si	(6×)	3·296 (1)
K(2)——Mg(1)	(2×)	3·538
Mg(1)-Mg(2)	(3×)	2·951
Mg(1)-Si	(6×)	3·482 (1)
Mg(2)-Si	(4×)	3·050 (1)
Si——Si	(2×)	3·148 (1)
Si——Si		3·181 (1)
D——O(1)	(6×)	3·420 (3)
D——O(2)	(12×)	3·249 (2)
E——O(1)	(2×)	2·170 (2)
E——O(3)	(4×)	2·900 (2)
E——O(2)	(4×)	3·293 (2)
E——O(1)	(2×)	3·399 (3)

H_2O molecules are located near the D sites in osumilite. But this conclusion was based on their faulty chemical analysis and is no longer tenable (personal communication of Brown & Gibbs to Olsen & Bunch, 1970). One could also consider the vicinity of the E sites as a possible location for either cations or water molecules even though these sites are not occupied either in $K_2Mg_5Si_{12}O_{30}$ or in osumilite. However because of the

peculiar irregular shape of the coordination around E (Table 4) this does not appear to be a very likely coordination site.

The general crystal chemical formula of milarite-type phases can therefore be written as $A_2^{[6]}B_2^{[9]}C^{[12]}D^{[18]}T2_3^{[4]}T1_{12}^{[4]}O_{30}$. The D sites have been included in the general formula even though no proof exists presently that they are occupied in any milarite group structure; however it seems to be a reasonable place for a large atom. The E sites have been excluded from the formula. It is to be understood that the coordination polyhedra around the B sites and the D sites may vary from one milarite-type compound to the other. These coordinations consist of two crystallographically distinct oxygen atoms. The shapes and dimensions [see Table 4(e)] of these coordination polyhedra are influenced mainly by the size of the atom occupying the B sites. A cation such as K would displace the O(1) atom towards D as discussed previously and influence the shape of the coordination polyhedron around the D sites. A similar consideration is true for the E sites.

The K–O distances are of the usual length (Table 4). The octahedral Mg(1)–O(3) distance of 2·10 Å is dis-
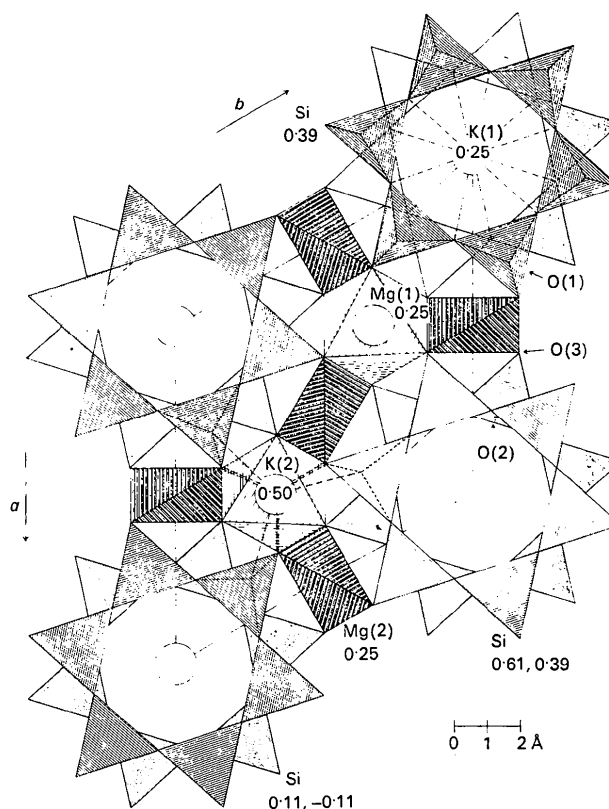

Fig. 1. $K_2Mg_5Si_{12}O_{30}$, view parallel to [001]. The K atoms are shown as circles, their bonds to the oxygen atoms as broken lines. The remainder of the structure is shown in polyhedral representation. The heights of some cations are indicated in fractional coordinates. Each type of oxygen atom is identified once by an arrow pointing to it.

tinctly longer than the average of 123 Mg–O distances of 2·085 Å reported by Baur (1970). The tetrahedral Mg(2)–O(3) distance of 1·955 Å agrees well with the value of 1·88 Å found by Smith (1953) in melilite if one considers that this is an (Mg, Al)–O bond. It is also in good agreement with the distances given for tetrahedral magnesium in spinel-phases: 1·944 Å in $MgAl_2O_4$ (Zorina & Kvitka, 1969) and 1·964 Å in MgV_2O_4 (Plumier & Tardieu, 1963). The angles around Mg(2) deviate very considerably from the ideal tetrahedral values [Table 4(c)]. The individual Si–O distances in the T1 tetrahedron [Table 4(d)] are significantly different from the mean value of the Si–O bond length in equipoint T1. These deviations from the mean correlate reasonably well with the Pauling bond strengths received by the individual oxygen atoms (Table 5). In Table 6 we present the calculation of the individual Si–O bond lengths based on the mean Si–O distance and the deviations of the individual bond strengths from the mean bond strength in the tetrahedron (rule 3; Baur, 1970). This approach allows us to understand in a semiquantitative way the differences between the bond lengths in the T1 tetrahedra in $K_2Mg_5Si_{12}O_{30}$ and in osumilite. In $K_2Mg_5Si_{12}O_{30}$, where T2 is occupied by Mg^{2+}, the O(3) atom is undersaturated (1·89 v.u.). In osumilite, Al^{3+} and Fe^{3+} occupy T2 and consequently O(3) is slightly oversaturated (2·04 v.u.). The difference in O(3) bond saturation is nicely reflected in the observed bond lengths. The Δd's indicate that in

$K_2Mg_5Si_{12}O_{30}$ about one half of the variation in bond lengths can be attributed to the Δp_0 of the individual oxygen atoms. In osumilite the agreement is even better, particularly if one considers the higher values of the e.s.d.'s of the Si–O bond lengths. The mean Δd's observed in these two cases are similar to those found for a larger sample in similar calculations for other silicates (Baur, 1971).

All atoms except the O(3) oxygen atom display a more or less anisotropic behavior (Table 7). The largest axes of the thermal ellipsoids of the atoms K(1), K(2) and Mg(1) are parallel to the c axis. This is reasonable because it is the direction in which the cations are allowed the largest vibration by the arrangement of the surrounding oxygen atoms. Similarly it is plausible that the largest motion of Mg(2) takes place in a plane normal to the long axis of the distorted coordination tetrahedron. The longest axis of the thermal ellipsoid of the Si atom is approximately in the plane (001) pointing radially out of the center of the hexagonal ring of tetrahedra. The long axes of the strongly anisotropic motions of atoms O(1) and O(2) are in both cases in the planes normal to the vector connecting the two Si atoms to which these oxygen atoms are bonded. This motion reflects the strong bonding to the silicon atoms. The weak bonds to K(1) and K(2) obviously do not influence the thermal motion of O(1) and O(2). The case is different for oxygen atom O(3), which is coordinated approximately trigonally by Si, Mg(1) and

Table 5. *Electrostatic bond strengths* (p_0) *received by the oxygen atoms*

(a) In $Mg_2[^6]K[^9]K[^{12}]Mg_3[^4]Si_{12}O_{30}$

	K(1)[^{12}]	K(2)[^9]	Mg(1)[^6]	Mg(2)[^4]	Si	$\Sigma = p_0$
O(1)		$\frac{1}{18}$			$2 \times 1·00$	2·06 v.u.
O(2)	$\frac{1}{12}$				$2 \times 1·00$	2·08
O(3)		$\frac{1}{18}$	$\frac{2}{6}$	$\frac{2}{4}$	1·00	1·89

(b) In Osumilite, $(Mg, Fe^{2+})_2[^6](K, Na)[^{12}](Al, Fe^{3+})_3[^4](Si_{0.85}Al_{0.15})_{12}O_{30}$ (Brown & Gibbs, 1969)

	K, Na	Mg, Fe^{2+}	Al, Fe^{3+}	Si, Al	$\Sigma = p_0$
O(1)				$2 \times 0·96$	1·92 v.u.
O(2)	$\frac{1}{12}$			$2 \times 0·96$	2·00
O(3)		$\frac{2}{6}$	$\frac{3}{4}$	0·96	2·04

Table 6. *Observed and calculated* Si–O *bond lengths*

The calculation is based on $d_{calc} = (d_{obs, mean} + 0·091\Delta p_0)$Å (Baur, 1970). ($d_{obs}$ = observed interatomic distance, $\Delta d = d_{obs} - d_{calc}$, v.u. = valence units).

(a) $K_2Mg_5Si_{12}O_{30}$

	p_0	Δp_0	d_{calc}	d_{obs}	Δd
Si–O(1)	2·06 v.u.	0·03 v.u.	1·616 Å	1·613 (1) Å	−0·003 Å
Si–O(2)	2·08	0·05	1·618	1·625 (2)	0·007
Si–O(2)	2·08	0·05	1·618	1·630 (2)	0·012
Si–O(3)	1·89	−0·14	1·600	1·585 (2)	−0·015
mean:	2·03			1·613	0·009

(b) Osumilite

	p_0	Δp_0	d_{calc}	d_{obs}	Δd
T1–O(1)	1·92 v.u.	−0·07 v.u.	1·621 Å	1·621 (3)	0·000 Å
T1–O(2)	2·00	0·01	1·628	1·616 (5)	−0·012
T1–O(2)	2·00	0·01	1·628	1·640 (5)	0·012
T1–O(3)	2·04	0·05	1·632	1·632 (5)	0·000
mean:	1·99			1·627	0·006

Mg(2) and in addition by K(2). Atom O(3) appears therefore to be locked in, which is reflected in the fact that the amplitude of its thermal motion is the smallest of the three oxygen atoms and that its motion seems to be isotropic within the limits of error. The details of the orientation of the thermal ellipsoids thus are in qualitative agreement with the geometrical arrangements in this crystal structure.

Table 7. $K_2Mg_5Si_{12}O_{30}$, root-mean-square thermal displacements along principal axes and their orientations relative to a, b and c

	Axis	Displacement	Angle with axis [100]	[010]	[001]
K(1)	1	0·111 (4) Å	–	–	90°
	2	0·111	–	–	90
	3	0·154 (5)	90°	90°	0
K(2)	1	0·106 (5)	–	–	90
	2	0·106	–	–	90
	3	0·136 (6)	90	90	0
Mg(1)	1	0·077 (5)	–	–	90
	2	0·077	–	–	90
	3	0·119 (5)	90	90	0
Mg(2)	1	0·087 (6)	90	30	90
	2	0·112 (4)	90	90	0
	3	0·116 (5)	0	120	90
Si	1	0·088 (2)	68 (34)	87 (16)	28 (29)
	2	0·090 (2)	157 (32)	64 (5)	67 (33)
	3	0·109 (2)	98 (5)	26 (5)	104 (5)
O(1)	1	0·095 (6)	90	90	0
	2	0·155 (6)	32 (85)	152 (85)	90
	3	0·158 (5)	58 (85)	62 (85)	90
O(2)	1	0·105 (5)	27 (5)	145 (4)	81 (7)
	2	0·132 (4)	78 (8)	91 (8)	166 (8)
	3	0·157 (4)	67 (4)	55 (4)	79 (8)
O(3)	1	0·108 (5)	99 (32)	21 (29)	96 (21)
	2	0·113 (5)	158 (27)	73 (34)	109 (24)
	3	0·121 (4)	110 (24)	78 (17)	20 (23)

References

BAUR, W. H. (1970). Trans. Amer. Cryst. Assoc. **6**, 129.
BAUR, W. H. (1971). Amer. Miner. **56**, 1573.
BAUR, W. H. & KHAN, A. A. (1970). Acta Cryst. B**26**, 1584.
BROWN, G. E. & GIBBS, G. V. (1969). Amer. Miner. **54**, 101.
DODD, R. R., VAN SCHMUS, W. R. & MARVIN, U. B. (1965). Science, **149**, 972.
FORBES, W. C. (1972). Miner. Mag. In the press.
ITO, T., MORIMOTO, N. & SADANAGA, R. (1952). Acta Cryst. **5**, 209.
MIYASHIRO, A. (1956). Amer. Miner. **41**, 104.
OLSEN, E. (1967). Amer. Miner. **52**, 1519.
OLSEN, E. & BUNCH, T. E. (1970). Amer. Miner. **55**, 875.
PASHEVA, Z. P. & TARKHOVA, T. N. (1953). Dokl. Akad. Nauk SSSR, **88**, 807.
PLUMIER, R. & TARDIEU, A. (1963). C. R. Acad. Sci. Paris, **257**, 3858.
ROEDDER, E. W. (1951). Amer. J. Sci. **249**, 81, 774.
SEIFERT, F. & SCHREYER, W. (1969). Contr. Mineral. Petrol. **22**, 190.
SMITH, J. V. (1953). Amer. Miner. **38**, 643.
ZOLTAI, T. (1960). Amer. Miner. **45**, 960.
ZORINA, N. G. & KVITKA, S. S. (1969). Sov. Phys. Crystallogr. **13**, 599

The Crystal Structures of Polymorphs I and III of Sulphathiazole

BY G. J. KRUGER AND G. GAFNER

Chemical Physics Group, National Physical Research Laboratory, Council for Scientific & Industrial Research, P.O. Box 395, Pretoria, South Africa

The crystal structure of sulphathiazole II is known. The crystal structures of the other two known crystalline forms of sulphathiazole (N'-2-thiazolylsulphanilamide) have now been determined and are reported. The intensities were measured using Mo $K\alpha$ radiation and an automatic diffractometer. The structures were solved by the application of the Karle–Hauptman Σ_2 relationship and refinement was done by full-matrix least-squares methods. The main differences between the polymorphs of sulphathiazole lie in the hydrogen bonding and its effects on the arrangement of the molecules in the crystals.

Introduction

In the paper reporting the structure determination of sulphathiazole II (Kruger & Gafner, 1972) crystallographic data for the other two known polymorphs, modifications I and III, were listed. This information is repeated here in Table 1. In order to investigate the structural differences involved in the polymorphism of sulphathiazole, the crystal structures of sulphathiazole I and III have now been determined.