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The Crystal Structure of Milarite

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The crystal structure of milarite has been worked out using oscillation and Weissenberg photographs (Co $K\alpha$, $\lambda = 1{\cdot}79$ Å). The unit cell has $a = 10{\cdot}54$, $c = 13{\cdot}96$ Å, and contains one molecule of $K_2Ca_4Be_4Al_2Si_{24}O_{60}.H_2O$. The space group is D_{6h}^2–$C6/mcc$. The structure may be described as composed of the double hexagonal rings, $(Be_{0\cdot10}Si_{0\cdot90})_{12}O_{30}$, held together by $(Be_{0\cdot27}Al_{0\cdot33}Si_{0\cdot40})$ atoms on the one hand and by K and Ca atoms on the other; or alternatively as a three-dimensional net-work, $(Be_{0\cdot27}Al_{0\cdot33}Si_{0\cdot40})_6(Be_{0\cdot10}Si_{0\cdot90})_{24}O_{60}$, of linked Be, Al, Si–O and Be, Si–O tetrahedra, reinforced by K and Ca atoms. Potassium is surrounded by twelve oxygen atoms, of which six belong to one double ring and the remaining six to another. Calcium is surrounded by six oxygen atoms, one each from six neighbouring double rings. Water molecules lie inside the ring, only half of the available space being filled by them. An oxygen atom is either between two $(Be_{0\cdot10}Si_{0\cdot90})$ atoms and one K atom or between one $(Be_{0\cdot10}Si_{0\cdot90})$ atom, one $(Be_{0\cdot27}Al_{0\cdot33}Si_{0\cdot40})$ atom and one Ca atom.

Although milarite, on account of its anomalous optical properties, has been the object of considerable discussion, it was comparatively lately that its chemical constitution was correctly interpreted by Palache (1931), who found the existence in it of beryllium as a main component. The chemical formula, $K_2Ca_4Be_4Al_2Si_{24}O_{60}.H_2O$ as deduced by him, seems to suggest that beryllium plays structurally the same part as silicon and aluminium. The present study was undertaken to enquire if this is so.

1. Experimental

The specimens used, pale green transparent hexagonal prisms measuring 1×1×3 mm., came from Val Giuf, Grisons, Switzerland, the well-known and almost unique locality of the mineral. A thin slip parallel to (00.1) was cut from the specimens and mounted on a crystal-holder capable of transverse movement. This enabled us to focus the fine X-ray beam on to any portion of the slip without disturbing its setting.

Co $K\alpha$ radiation ($\lambda = 1{\cdot}79$ Å) was used throughout the experiments, in which Weissenberg–Buerger as well as oscillation photographs were taken. The intensities of reflexions were estimated visually and converted into numerical values on an arbitrary scale. They were corrected for the Lorentz and polarization factors, but not for extinction nor absorption. At the final stage of analysis these values were rendered comparable with the absolute ones by multiplying by a proportionality factor which minimizes the sum of differences between F_o and F_c for the arbitrarily selected reflexions (20.0), (30.0), (70.0) and (90.0).

2. Unit cell and space group

The hexagonal unit cell has the dimensions:

$$a = 10.54,\ c = 13.96\ \text{Å}\,.$$

There is one molecule of $K_2Ca_4Be_4Al_2Si_{24}O_{60}.H_2O$ in the cell, the density being 2.46 g.cm.$^{-3}$ calculated compared with 2·55–2·59 g.cm.$^{-3}$ measured (Dana, 1904, p. 312). Assuming holohedral symmetry, the space group is D_{6h}^2–$C6/mcc$, the reflexions $(hh.l)$ and $(h0.l)$ being observed only when l is even. These results are in agreement with those obtained by Gossner (1930).

An examination by X-rays, it is to be noted, revealed that the optically differently oriented sectors, which under the polarizing microscope present an appearance of a twin, constitute in reality a perfect single crystal, there being no difference between them in crystallographic orientation. The twin-like behavior of milarite, therefore, may be interpreted as twinning in the incipient stage, in which the localizing or ordering, or more probably deformation of electron configuration, of certain atoms occurs in such a way that a twin is simulated optically.

3. Analysis

If we ascribe to aluminium in milarite a four-coordination, the ratio of all four-coordinated metal (i.e. Be, Al and Si) to oxygen atóms is 1:2. This suggests that a structure of milarite may be conceived either on the basis of a silica-like three-dimensional net-work or of a 'felspar-like' two-dimensional double sheet, both formed of linked oxygen tetrahedra around a metal atom. The hexagonal symmetry, however, seems to favour the latter rather than the former scheme. Accordingly, we tried to place in the unit cell of milarite such double sheets as we have recently found in α-celsian (Ito, 1950, p. 19). It soon became clear, however, that, in order to satisfy the requirements of the space group, we must first break up these sheets, (Al, Be, Si)O_2, into their component double hexagonal rings, (Al, Be, Si)$_{12}O_{30}$, and then recombine them by joining them differently through other (Al, Be, Si) atoms which again occupy the centres of oxygen tetrahedra. The former (Al, Be, Si) atoms will, then, occupy the twenty-four-fold equivalent positions and the latter (Al, Be, Si) atoms the six-fold equivalent positions. The resulting arrangement has dimensions nearly equal to those of milarite and is a network of composition (Al, Be, Si)O_2 with enough room left for other atoms to be accommodated. Since this explains the observed reflexions roughly, we assumed it to be the framework underlying the structure of milarite and determined the parameters of all the atoms it contains as usual by trial and error. That aluminium atoms can enter into the six-fold equivalent positions only is inferred from the interatomic distances. Silicon and beryllium, on the contrary, divide between them the rest of the six-fold and a set of twenty-four-fold equivalent points. If we put all twenty-four silicon atoms in the unit cell into twenty-four-fold positions, there would be no valency left for those oxygen atoms of the ring which are to match the bonds from potassum atoms. For the distribution of beryllium and silicon atoms over these six-fold and twenty-four-fold equivalent positions, the interatomic distances were again taken into account. The charge of (Al, Be, Si) and (Be, Si) atoms has been so determined that the bonds between them and the intervening oxygen atom are inversely proportional to the square of the respective distances.

The double Fourier synthesis on (00.1) was utilized for the successive refinement of atomic positions.

Table 1. *Coordinates of atoms*

Atom	No. of the equivalent atoms in the cell	x/a	y/b $(b = a)$	z/c
Be, Si	24	0·745	0·076	0·111
Be, Al, Si	6	$\frac{1}{2}$	0	$\frac{1}{4}$
K	2	0	0	$\frac{1}{4}$
Ca	4	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$
O_I	12	0·703	0·091	0
O_{II}	24	0·916	0·199	0·128
O_{III}	24	0·653	0·120	0·185
H_2O	1	0	0	0

Table 2. *The reliability factors*

$hk.l$	No. of reflexions observed	$R = \frac{\lvert\lvert F_o - F_c\rvert\rvert}{\lvert F_o\rvert}$
$00.l$	7	0·33
$hk.0$	43	0·26
$hh.l$	35	0·33
$hk.l$	128	0·30

In Table 1 are given the parameters of atoms, in Table 2 the reliability factors of the structure for the various categories of reflexions and in Table 3 a comparison of F_o and F_c.

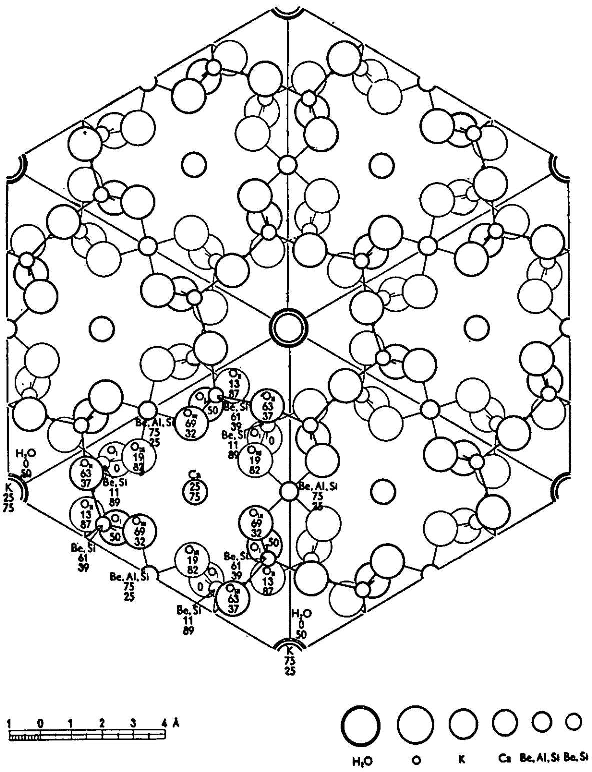

Fig. 1. The structure of milarite, projected on (00.1). The height of each atom is given by a percentage of the c translation. (Be, Si)–O and (Be, Al, Si)–O linkages are indicated.

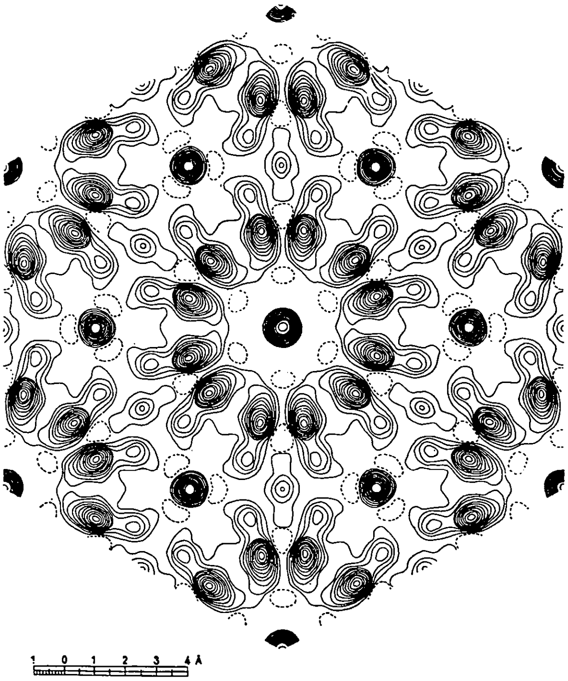

Fig. 2. Fourier projection of electron density in milarite. The projection corresponds to Fig. 1. Contours at intervals of 5 e.Å^{-2}, the zero-electron level being broken.

Table 3. *Comparison of.* F_o *and* F_c

hk.l	F_o	F_c
00.2	180	−147·0
00.4	170	−145·5
00.6	32	−46·7
00.8	190	298·6
0,0,.,10	84	106·8
0,0,.,12	10	− 5·4
0,0,.,14	152	−201·6
10.0	—	25·8
20.0	90	−51·9
30.0	136	158·3
40.0	0	11·2
50.0	180	−184·9
60.0	20	21·5
70.0	100	−96·6
80.0	0	− 5·1
90.0	74	69·8
11.0	120	−111·9
22.0	142	124·3
33.0	82	−61·9
44.0	20	− 4·1
55.0	184	181·4
21.0	20	8·3
31.0	78	76·4
32.0	24	−21·6
41.0	98	108·3
42.0	58	72·5
43.0	0	−20·4
51.0	0	7·4
52.0	192	164·3
53.0	44	−29·6
54.0	0	−29·9
61.0	0	43·9
62.0	104	123·3
63.0	0	8·2
64.0	0	20·0
71.0	0	17·3
72.0	0	25·2
73.0	0	−37·2
81.0	0	− 1·6
8,2,.,0	100	100·5
21.1	125	−121·7
31.1	51	−74·7
32.1	45	47·3
41.1	44	37·6
42.1	98	85·6
43.1	41	48·2
51.1	0	5·4
52.1	50	28·4
53.1	0	− 5·1
54.1	24	27·0
61.1	66	70·6
62.1	100	−83·2
63.1	0	−16·9
64.1	52	39·0
71.1	0	4·6
72.1	28	27·7
73.1	0	6·0
81.1	80	74·8
82.1	0	·4
20.2	62	−77·1
21.2	25	25·5
30.2	0	− 9·9
31.2	0	19·8
32.2	0	− 7·9
40.2	0	−26·6
41.2	98	−94·1
42.2	0	3·8
43.2	20	23·8
50.2	0	17·4
51.2	40	45·2
52.2	0	−10·6
53.2	0	11·0
54.2	0	35·7
60.2	130	−135·9
61.2	0	7·9
62.2	30	−43·8
63.2	62	−57·5
64.2	0	−26·5
70.2	0	10·5
71.2	0	−18·0
72.2	0	15·0
73.2	0	4·4
80.2	0	39·4
81.2	0	18·3
82.2	45	−59·8
21.3	65	57·7
31.3	30	−43·1
32.3	24	−22·4
41.3	0	− 9·0
42.3	25	−24·6
43.3	50	−49·9
51.3	39	−31·3
52.3	0	8·9
53.3	0	14·8
54.3	0	·8
61.3	20	28·6
62.3	100	90·7
63.3	38	−35·8
64.3	20	−16·4
71.3	0	37·7
72.3	53	−60·0
73.3	0	−21·7
81.3	58	−43·1
82.3	0	− 6·6
20.4	140	156·0
21.4	29	24·6
30.4	31	30·7
31.4	73	−86·0
32.4	0	− 1·6
40.4	0	− 6·1
41.4	82	87·2
42.4	28	47·8
43.4	0	3·5
50.4	85	77·7
51.4	0	3·2
52.4	68	−65·8
53.4	0	−12·8
54.4	0	27·0
60.4	140	152·7
61.4	50	−50·1
62.4	50	−43·2
63.4	68	62·9
64.4	0	8·7
70.4	80	67·2
71.4	100	66·2
72.4	0	1·2
80.4	70	71·8
81.4	0	−21·3
21.5	23	−48·9
31.5	108	104·8
32.5	0	22·2
41.5	27	−29·8
42.5	100	−107·4
43.5	0	− 7·7
51.5	29	−36·4
52.5	0	− 7·6
53.5	22	24·1
54.5	30	−21·3
61.5	100	108·2
62.5	55	45·8
63.5	0	− 7·0
64.5	84	−55·6
71.5	0	30·3
72.5	0	−24·3
81.5	100	−92·2
11.2	98	−108·7
11.4	174	165·6
11.6	72	−54·2
11.8	20	−33·4
1,1,.,10	84	−116·6
1,1,.,12	30	81·8
22.2	66	−94·0
22.4	42	63·4
22.6	86	−142·8
22.8	94	158·0
2,2,.,10	70	−96·6
2,2,.,12	0	41·2
33.2	50	43·7
33.4	112	110·8
33.6	22	−60·2
33.8	0	22·1
3,3,.,10	76	−85·1
44.2	100	−91·5
44.4	174	209·3
44.6	30	−28·0
44.8	0	19·9
5,5,.,2	0	−55·2
5,5,.,4	0	−56·6

4. Description of structure

The structure of milarite is shown in Fig. 1, projection (00.1), and the corresponding Fourier projection of electron density in Fig. 2.

Whereas only beryllium and silicon atoms occupy the centres of the oxygen tetrahedra which form the double hexagonal rings, aluminium as well as beryllium and silicon atoms occupy the centres of those oxygen tetrahedra which hold these rings together, the ratio being Be:Si = 10:90 in the former positions and Al:Be:Si = 33:27:40 in the latter. The structure, therefore, may be described as composed of $(\mathrm{Be}_{0\cdot10}\mathrm{Si}_{0\cdot90})_{12}\mathrm{O}_{30}$ rings linked by $(\mathrm{Be}_{0\cdot27}\mathrm{Al}_{0\cdot37}\mathrm{Si}_{0\cdot40})$ atoms on the one hand and by potassium and calcium atoms on the other (Fig. 3); or, alternatively, as a three-dimensional $(\mathrm{Be}_{0\cdot27}\mathrm{Al}_{0\cdot33}\mathrm{Si}_{0\cdot40})_6(\mathrm{Be}_{0\cdot10}\mathrm{Si}_{0\cdot90})_{24}\mathrm{O}_{60}$ network reinforced by potassium and calcium atoms. (The form of the double ring is somewhat different from the ideal one with which analysis was started.)

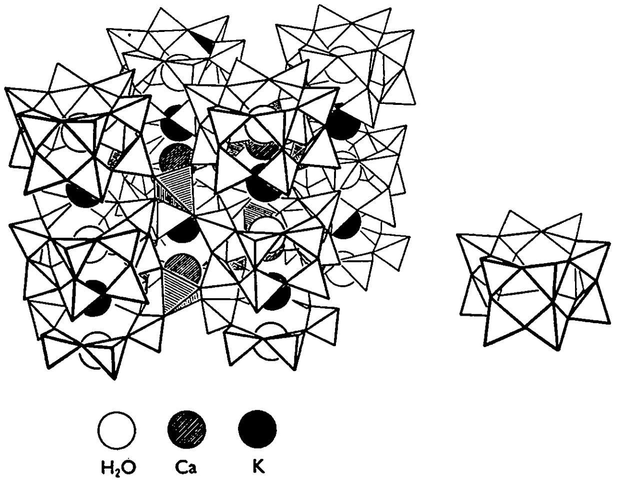

Fig. 3. The structure of milarite illustrated as linked oxygen tetrahedra around (Be, Si) or (Be, Al, Si) atoms. The double hexagonal ring, $(\mathrm{Be, Si})_{12}\mathrm{O}_{30}$, can be clearly seen. (Be, Al, Si)–O tetrahedra which bind the rings together are shaded. (A double ring is shown separately to make the reading of the figure easier.)

Potassium is co-ordinated by twelve oxygen atoms, of which six belong to one ring and the remaining six to another. Calcium is surrounded octahedrally by six oxygen atoms, one from each of six neighbouring rings. An oxygen atom is shared either by two $(\mathrm{Be}_{0\cdot10}\mathrm{Si}_{0\cdot90})$ atoms and one potassium atom or by one $(\mathrm{Be}_{0\cdot10}\mathrm{Si}_{0\cdot90})$ atom, one $(\mathrm{Be}_{0\cdot27}\mathrm{Al}_{0\cdot33}\mathrm{Si}_{0\cdot40})$ atom and one calcium atom. Water groups lie inside the double rings, being presumably held by a weak van der Waals force. Only one half of the total available space for water molecules is statistically filled by them. Therefore, it is possible under certain conditions that one more water molecule per cell is taken up without effect on the structure.

The balance of valency is illustrated in Fig. 4 and the interatomic distances are given in Table 4.

The present study was initially undertaken by one of the present writers (T.I.) in collaboration with

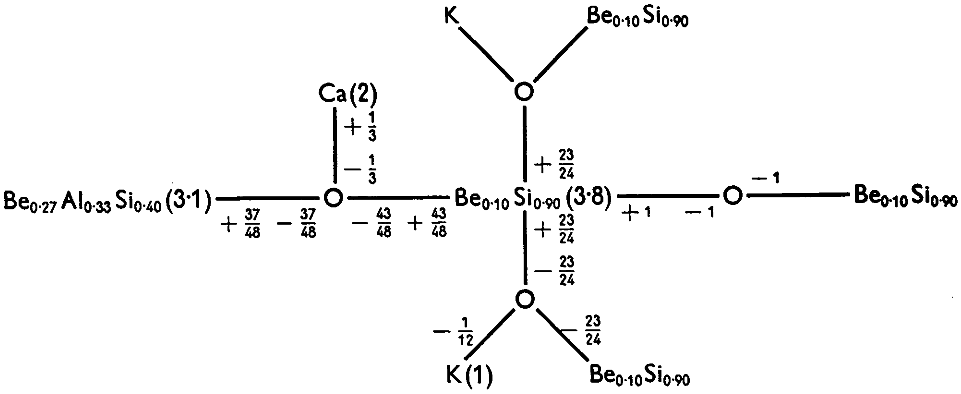

Fig. 4. Balance of valency in milarite. The distribution of beryllium and silicon atoms among (Be, Al, Si) and (Be, Si) positions is arbitrary within certain limits. The total charge of (Be, Al, Si) and of (Be, Si) atoms has been so determined that the bonds between them and the intervening oxygen atom are inversely proportional to the squares of the respective distances. Numbers in parenthesis indicate charge of atom.

Table 4. *Interatomic distances in milarite*

Atom	Neighbour*	Distance (Å)	Atom	Neighbour	Distance (Å)
Be, Si	O_I(1)	1·64	O_I	O_{II}	2·63
	O_{II}(2)	1·59		O_{III}	2·70
	O_{III}(1)	1·63			
			O_{II}	O_{II}	2·64
Be, Al, Si	O_{III}(4)	1·75		O_{III}	2·60
Ca	O_{III}(6)	2·35		O_{III}	2·66
K	O_{II}(12)	3·14			
			O_{III}	O_{III}	2·95
				O_{III}	2·67
				O_{III}	2·88

* Numbers in parenthesis indicate the equivalent atoms surrounding the central atom.

Y. Takéuchi and Y. Takano, whose contributions are appreciated.

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The Crystal Structure of Ti_3Au and Ti_3Pt

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Powder patterns indicate that Ti_3Au and Ti_3Pt crystallize in the *A*15 (β-wolfram) structure with lattice parameters of 5·096 and 5·033 Å, respectively.

An exploratory X-ray investigation of the titanium–gold and titanium–platinum systems revealed the presence of intermediate phases in the vicinity of the compositions Ti_3Au and Ti_3Pt. The crystal structures of these new phases were worked out from powder patterns and are described in the present note.

The alloys were prepared by rolling suitable amounts of the constituent metals into thin flat strips, which were then wrapped together and arc melted in an atmosphere of high-purity helium by a technique which has been described elsewhere (Schramm, Gordon & Kaufmann, 1950). The gold and platinum were 'commercially pure' grade (i.e. at least 99·9% pure) and the titanium (prepared by the iodide decomposition process) contained less than 0·05% total impurities by the vendor's analysis.

After arc melting, the Ti_3Au specimen was sealed in an evacuated silica tube and heated for 75 hr. at 1500° F. The Ti_3Pt specimen was not given any further heat treatment. Both specimens were crushed, and portions of the resulting powders which passed through a 200 mesh screen were used to obtain X-ray diffraction patterns with a camera of 14·32 cm. diameter and copper $K\alpha_1$ radiation.

The powder patterns thus obtained were easily indexed as those of simple cubic lattices having parameters of 5·096 Å for the Ti_3Au and 5·033 Å for the Ti_3Pt. These values of the parameters were computed by applying Cohen's (1935) least-squares method to the last ten back-reflection lines of each pattern. The possibility that the structure of these compounds (which the powder patterns showed at once to be isomorphous) is the *A*15 or β-wolfram structure was suggested by the AB_3 atomic ratio, by the positions of the constituent metals in the periodic table, and by the fact that reflections of the type (*hhl*) with odd *l* are missing, as required by the space group O_h^3 of the *A*15 structure. Accordingly, relative intensities were computed by the formula

$$I \propto p|F|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta},$$

where *p* is the planar multiplicity factor, *F* is the structure factor, and the angular factor represents the

Table 1. *Diffraction data for* Ti_3Au

hkl	I_o Film	I_o Spectrometer	I_c
110	*w*	630	764
200	*w*	520	424
210	*vw*	250	192
211	*m*	1000	1000
220	*vw*	150	118
310	*w*	200	165
222	—	—	8
320	*vw*	60	36
321	*ms*	640	475
400	*w*	150	87
411, 330	*w*	140	97
420	*mw*	170	137
421	*vvw*	—	8
332	*mw*	—	123
422	*vw*	—	47
510, 431	*mw*	—	136
520, 432	*vw*	—	39
521	*m*	—	215
440	*mw*	—	103
530, 433	*mw*	—	104
600, 442	*m*	—	168
610	*vvw*	—	17
611, 532	*s*	—	460
620	*vw*	—	84
541	*m*	—	258

s=strong; *ms*=medium strong; *m*=medium; *mw*=medium weak; *w*=weak; *vw*=very weak; *vvw*=very very weak.

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