Ann. Rep., Inst. Geosci., Univ. Tsukuba, no. 15, pp. 92-95, Dec. 25, 1989

The crystal structure of milarite : Two split-site model

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Introduction

Milarite is a framework silicate mineral with the general formula

$(K, Na)\ Ca_2[(Be_2Al)Si_{12}O_{30}].xH_2O \quad x \sim 3/4$

It is generally found in pegmatitic granites and granitic pegmatites, and shows significant variations in chemical composition along with variation in paragenetic sequence and geographic locality. Milarite is possibly much more common than is generally realized, as it can be mistaken for quartz in hand specimen. It is the prototype mineral for a large structural group that includes osumilite. The milarite structure is extremely flexible from a chemical viewpoint, and a considerable number of minerals adopt this basic atomic arrangement. In particular, it seems to be a structure type that is favoured by the light lithophile elements.

The present study addresses the problem of two split-sites in milarite by focusing on two related issues : (1) the stereochemical variations across the widened range of the chemical composition and (2) the cause of the optical anomaly.

Sample description

The sample used occurs as fine crystals in low-temperature hydrothermal pegmatitic veins in the granites of Tittling, Bavaria, Germany (Tennyson, 1960). The chemical composition, as shown in Table 1, was analyzed by Jarosewich in 1971 and the other physical properties were described by Cerny *et al*. (1980). The optical observation reveals a sector-zoning and moire. This milarite is extremely rich in Be, namely 6.71%.

Table 1. Chemical compositson of milarite.

Weight %		Number of ions		
SiO_2	70.65	Si	$T(1)_{24}$	23.51
Al_2O_3	4.34	Al^{3+}	$T(2)_6$	4.34
BeO	6.71	Be		5.35
MnO	<.01			
CaO	10.80	Ca^{2+}	A_4	3.85
Na_2O	.52	K	C_2	2.00
K_2O	4.97	Na		0.35
H_2O^-	.15	K	B_4	0.11
H_2O^+	1.29	H_2O		1.43
Total	99.43			

X-ray data collection

Crystals for intensity data collection were selected on the basis of optical clarity, homogeneity, freedom from inclusions, and equant shape. The crystals were mounted on a Nicolet R3M automated four-circle diffractometer, and twenty-five intense reflections were centered using graphite-monochromated MoKα radiation. Least-squares refinement of the setting angles produced the (hexagonally constrained) cell dimensions given in Table 2. Reflections were collected out according to the experimental procedure of Hawthorne (1985) ; the other miscellaneous information pertinent to X-ray data collection and structure refinement is given in Table 2. Ten strong reflections uniformly distributed with regard to two-theta were measured at 10° intervals psi (the azimuthal angle corresponding to rotation of crystal about its diffraction vector) from 0 to 350°. These data were used to calculate an ellipsoidal shape for the crystal which was then used for absorption corrections on the whole intensity data set ; azimuthal R indices were 1.3%. Data were then corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors.

Table 2. Miscellaneous information for milarite refinements.

a (Å)	10.404(2)
c (Å)	13.825(5)
v ($Å^3$)	1296.0(7)
Sp. Gr.	P6/mcc
Z	2
Crystal size (mm)	0.20 × 0.24 × 0.36
Radiation	MoKα
Mono	Graphite
Raz %	1.4
Total |F|	1521
No of |F|	581
Ris %	4.6
Ran %	3.1

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Structure refinement

Scattering curves for neutral atoms together with anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (1974). The SHELXTL system of programs (Sheldrick, 1981) was used for the computational procedures.

Refinements were initiated using the atomic positions of milarite from King's Mountain (Cerny *et al.*, 1981) together with site-occupancies suggested by typical chemistries of the species concerned. Full-matrix refinement of all variables for an isotropic displacement model converged to R indices of about 4.3% (Table 2). Upon conversion to an anisotropic displacement model, the A cation (s) showed exaggerated anisotropy. This was taken as evidence for significant displacement of the cation off the special position; this was modeled as a split site with an isotropic displacement factor. The site of B cation (s) also was modeled as of a similar splitting type. These gave the same R indices as were obtained for the ordered anisotropic displacement model, but we prefer the split-site model on physical grounds; both models gave consistent results across the

Table 3. Final atomic parameters for milarite.

atom	X	Y	Z	Ueq (×10^4)
A	1/3	2/3	0.2437(4)	154(4)
B	1/3	2/3	0.0349(15)	585(77)
C	0	0	1/4	190(6)
T(1)	0.08168(7)	0.33625(8)	0.11257(4)	88(2)
T(2)	0	1/2	1/4	90(10)
O(1)	0.0946(4)	0.3830(3)	0	190(11)
O(2)	0.1951(2)	0.2759(2)	0.1340(1)	167(7)
O(3)	0.1154(2)	0.4729(2)	0.1804(1)	120(6)

atom	U11	U22	U33	U12	U13	U23
A	154(4)	(Ueq)	/	/	/	/
B	427(70)	427	900(185)	213(35)	/	/
C	183(7)	183	204(10)	91(4)	/	/
T(1)	87(3)	103(3)	73(2)	47(3)	−3(2)	−7(2)
T(2)	98(15)	93(11)	81(13)	49(7)	/	/
O(1)	298(16)	208(13)	68(9)	129(12)	/	/
O(2)	169(9)	230(10)	162(8)	145(8)	−22(7)	−24(8)
O(3)	131(8)	125(8)	112(7)	70(7)	−6(7)	−24(7)

$U_{ij} = U_{ij} \times 10^4$

Table 4. Selected interatomic distances (Å) and angles (°) in milarite.

A-O(3)	×3	2.310(2)	T(1)-O(1)	1.616(1)
A-O(3)a	×3	2.411(2)	T(1)-O(2)	1.617(3)
⟨A-O⟩		2.361	T(1)-O(2)d	1.618(2)
			T(1)-O(3)	1.588(2)
B-O(1)	×3	2.790(4)	⟨T(1)-O⟩	1.610
B-O(3)	×3	2.946(15)		
⟨B-O⟩		2.868	O(1)-T(1)-O(2)	109.0(2)
			O(1)-T(1)-O(2)d	109.9(1)
C-O(2)	×12	3.017(2)	O(1)-T(1)-O(3)	110.6(1)
			O(2)-T(1)-(2)d	104.3(1)
T(2)-O(3)	×4	1.670(2)	O(2)-T(1)-O(3)	111.2(1)
			O(2)d-T(1)-O(3)	111.6(1)
O(3)-T(2)-O(3)a	×2	102.9(1)	⟨O-T(1)-O⟩	109.4
O(3)-T(2)-O(3)e	×2	109.6(1)		
O(3)-T(2)-O(3)f	×2	116.2(1)		
⟨O-T(2)-O⟩		109.6		

series (Hawthorne *et al.*, unpublished). Full-matrix least-squares refinement of all variables (including site-occupancies) converged to the R index = 3.1%. Final atomic parameters are given in Table 3, and structure factor tables are deposited; selected interatomic distances and angles are given in Table 4.

Structural discussion

In the Bragg classification of the silicates, milarite is considered as a double-ring structure. However, if the chemical identity of the tetrahedrally-coordinated cation is not consiered, as suggested by Zoltai (1960) and Liebau (1985), milarite has a tetrahedral framework structure. The framework consists of hexagonal $Si_{12}O_{30}$ double rings of silicate tetrahedra linked by both tetrahedrally coordinated T (2) cations and octahedrally coordinated A cations into a three-dimensional tetrahedral framework. Furthermore, each B site surrounded by nine oxygens is sandwiched between adjacent A octahedra; the C and D sites, respectively surrounded by twelve and eighteen oxygens, are alternating along the tunnels formed by the stacking of the double hexagonal silicate rings.

The important finding during refinement was that two split sites could be defined in the crystal structure of the present milarite (Fig. 1); crystallographically two *4(d)* sites are changed into *8(h)* positions, which is compatible with the space group *P6/mcc*. One split site is the positional displacement of the A atoms which accommodate Ca only, and the other is that of the B atoms which consists of Na, K and H_2O. In addition to the Ca disorder, partial occupation of H_2O at the B position has been recently demonstrated by refinement of the crystal structures of natural and dehydrated milarite at 100 K (Armbruster *et al.*, 1989). The disorder at the A and B sites seems to be an intrinsic feature of milarite, because this is closely related to the extreme flexibility of chemical composition of milarite-type minerals (Forbes *et al.*, 1972). According to investigations by Bakakin *et al.* (1975) and Cerny *et al.* (1980), for H_2O molecules also, a B′ site near B, rather than B itself, is found to be the correct location. Accuracy of their refinements, however, is not enough to discuss the crystal chemistry. Afterward the work by

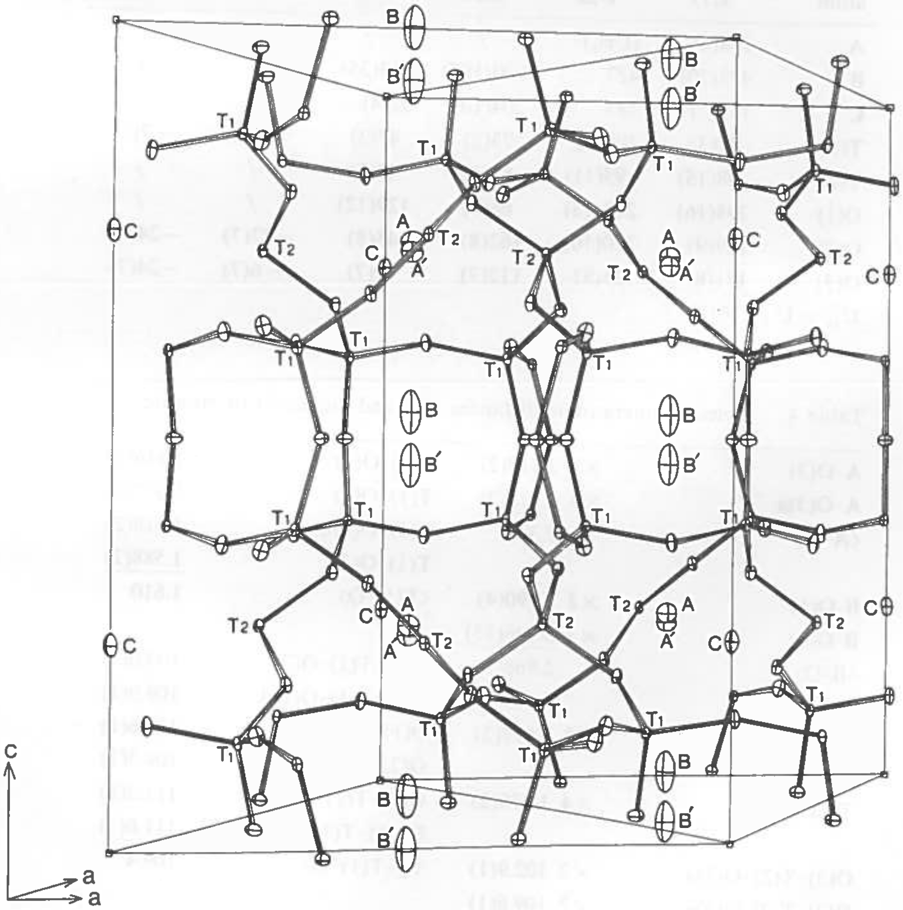

Fig. 1. Projection of the milarite structure on a plane 5° from (010). The probability ellipsoids of thermal vibration are shown together with T-O bond-sticks.

Abraham *et al*. (1983) has also shown that for some minerals of the milarite group, six-coordinated B′ sites near B, are available for full or partial occupation by Na and perhaps by H_2O molecules. As envisaged in high albite $NaAlSi_3O_8$ (Ribbe *et al*., 1969), exaggerated anisotropic vibration about a single center-of-motion of the Na atom is unlikely, and a split-atom model is more physically realistic. Splitting of the A site disorderingly occupied by Ca atoms is attributed to positional displacements caused largely by the difference in Al–O and Be–O bond lengths of T (2) sites and necessary adjustment of the positions of A atoms. Probably the thermal vibrations about the displaced atomic nodes are quite similar in size to those for atoms in the ordered counterpart. By contrast, the displacement of B site accommodating K, Na and H_2O represents the mean positions of these atoms ascribable to substitutional disorder of Al and Be cations at the T (2) sites. The structural flexibility modeled by split-sites of A and B atoms confirms that milarite can possess an extensive range of the coupled substitution, $Be^{T(2)}+Na^{B} \langle=\rangle Al^{T(2)}+[\,]^{B}$ or $Be^{T(2)}+Na^{B} \langle=\rangle Al^{T(2)}+H_2O$, with Be/(Be+Al) variable.

Milarite is known as a classic example of anomalous optical behavior (Cerny *et al*., 1980), but the question of the optical anomaly has remained largely dormant. In general, optical anomalies required lowering of symmetry. There are two important factors involved in reducing this symmetry ; (1) order/disorder of cations, and (2) the coupled substitution. Example of (1) are the ordering of octahedral cations, Al and Fe, in birefringent garnet (Takéuchi and Haga, 1976), and (F, OH) ordering in "anomalous" topaz (Parise *et al*., 1980). Milarite is an example of the latter. It is considered that larger distortion of the polyhedron accompanying the coupled substitution leads to local symmetry reduction at the *4*(*d*) site in the milarite structure. Therefore the present split model for milarite may be reasonable for deducing the symmetry that characterizes the optical anomaly.

A final conclusion is that the split-model proposed here has broader implications for (1) the coupled substitution ; (2) the optical anomaly ; and (3) the zonal structure. Work in progress persuades us that ease of structural accommodation for coupled substitutions is fundamental to the wide range of chemical variability of some minerals (e.g., tourmaline, apatite and titanite).

Acknowledgements

We acknowledge the technical assistance of Neil Ball, University of Manitoba, in operating the X-ray four-circle diffractometer.

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Key words : Milarite, crystal structure, split-site, coupled substitution, optical anomaly.