

THE CRYSTAL STRUCTURE OF DARAPIOSITE AND A COMPARISON WITH Li- AND Zn-BEARING MINERALS OF THE MILARITE GROUP

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ABSTRACT

By using material from a second occurrence of darapiosite in the Dara-i-Pioz alkaline massif, in northern Tajikistan, we have achieved a better characterization of this rare species belonging to the milarite group: a 10.262(2), c 14.307(1) Å, V 1305.0(3) Å³, space group $P6/mcc$, $(\text{Mn}_{1.54}\text{Zr}_{0.30}\text{Y}_{0.23}\text{Mg}_{0.03})_{\Sigma 2.10} (\text{Na}_{1.22}\text{K}_{0.36}\square_{0.42})_{\Sigma 2.00} \text{K}_{1.00} (\text{Li}_{1.53}\text{Zn}_{1.15}\text{Fe}^{2+}_{0.31})_{\Sigma 2.99} (\text{Si}_{11.98}\text{O}_{30.00})$, $Z = 2$, $\rho_{\text{meas}} = 2.93(3)$ g/cm³. The crystal structure has been refined to $R = 0.032$ from single-crystal X-ray data. Darapiosite is a double-ring silicate and is close to dusmatovite in chemical composition; Li dominates at the T2 site, which contains also Zn and Fe, and Na is the major cation at the B site. The presence of Li at T2 for the Li-bearing members of the milarite group is correlated with the dimensions of the cell parameters and of the coordination polyhedra. The occurrence of Zn at T2 further modifies relations between this site and other parts of the structure.

Keywords: darapiosite, crystal structure, milarite group, crystal chemistry.

SOMMAIRE

La découverte d'un second exemple de darapiosite au complexe alcalin de Dara-i-Pioz, dans le nord du Tadjikistan, a mené à une meilleure caractérisation de cette espèce rare, membre du groupe de la milarite: a 10.262(2), c 14.307(1) Å, V 1305.0(3) Å³, groupe spatial $P6/mcc$, $(\text{Mn}_{1.54}\text{Zr}_{0.30}\text{Y}_{0.23}\text{Mg}_{0.03})_{\Sigma 2.10} (\text{Na}_{1.22}\text{K}_{0.36}\square_{0.42})_{\Sigma 2.00} \text{K}_{1.00} (\text{Li}_{1.53}\text{Zn}_{1.15}\text{Fe}^{2+}_{0.31})_{\Sigma 2.99} (\text{Si}_{11.98}\text{O}_{30.00})$, $Z = 2$, $\rho_{\text{meas}} = 2.93(3)$ g/cm³. La structure cristalline a été affinée jusqu'à un résidu R de 0.032 à partir de données prélevées sur cristal unique. La darapiosite est un cyclosilicate à anneaux doubles, assez proche de la dusmatovite en composition chimique. Le Li est dominant dans le site T2, qui contient aussi Zn et Fe, et le Na est le cation le plus important à occuper le site B. La présence de Li au site T2 de la structure des membres du groupe de la milarite riches en Li a une répercussion dans les paramètres réticulaires et les polyèdres de coordination. La présence de Zn dans le site T2 contribue aussi à modifier les relations entre ce site et les autres parties de la structure.

(Traduit par la Rédaction)

Mots-clés: darapiosite, structure cristalline, groupe de la milarite, cristalochimie.

INTRODUCTION

Darapiosite from the alkaline massif of Dara-i-Pioz, in northern Tajikistan, was described by Semenov *et al.* (1975) as a new mineral with the ideal formula $\text{KNa}_2\text{Li}(\text{Mn,Zn})_2\text{ZrSi}_{12}\text{O}_{30}$. On the basis of the known data [chemical composition, X-ray powder-diffraction

pattern, a 10.32, c 14.39 Å, space group $P6/mcc$, physical properties and infrared (IR) spectrum], darapiosite belongs to the milarite group. Following a recent second finding of darapiosite, at the original locality, a complete characterization of darapiosite has been done; the results are reported here.

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OCCURRENCE

The type locality of darapiosite is a moraine of the Dara-i-Pioz glacier, on the southern slope of the Alai mountain ridge, Garm district, in northern Tajikistan. The glacial valley cuts the upper Dara-i-Pioz alkaline massif, which is related to the late Permian – early Triassic Alai intrusive complex. This massif consists of subalkaline granites and is a second-stage intrusion of the Turkestan complex; its central part consists of syenites and foyaites of the Alai complex, crossed by veins of syenite-aplites, pegmatites, quartz and carbonate. A widespread distribution of apgaitic accessory minerals enriched in Na, Ti, Nb, Ta, Zr, REE, Li, B is a characteristic of the massif.

The Dara-i-Pioz massif has become well-known in recent years because it has provided several new mineral species: tienshanite, $\text{BaNa}_2\text{MnTiB}_2\text{Si}_6\text{O}_{20}$ (Dusmatov *et al.* 1967), baratovite, $\text{KCa}_7(\text{Ti}, \text{Zr})_2\text{Li}_3\text{Si}_{12}\text{O}_{36}\text{F}_2$ (Dusmatov *et al.* 1975), cesium kupletskite, $(\text{Cs}, \text{K}, \text{Na})_3(\text{Mn}, \text{Fe}^{2+})_7(\text{Ti}, \text{Nb})_2\text{Si}_8\text{O}_{24}(\text{O}, \text{OH})_7$ (Yefimov *et al.* 1971), sogdianite, $(\text{Zr}, \text{Fe}^{3+}, \text{Ti}, \text{Fe}^{2+})_2(\text{Na}, \text{K}, \square)_2\text{K}(\text{Li}, \text{Al})_3[\text{Si}_{12}\text{O}_{30}]$ (Dusmatov *et al.* 1968), tadzhikite, $\text{Ca}_3(\text{Y}, \text{Ce})_2(\text{Ti}, \text{Al}, \text{Fe}^{3+})\text{B}_4\text{Si}_4\text{O}_{22}$ (Yefimov *et al.* 1970, Hawthorne *et al.* 1998). In particular, the following double ring silicates have been reported from the Dara-i-Pioz massif:

(1) five new species belonging to the milarite group: sogdianite (Dusmatov *et al.* 1968, Kabalov *et al.* 1993), darapiosite (Semenov *et al.* 1975), dusmatovite, $(\text{Mn}, \text{Zr}, \text{Y})_2(\square, \text{Na}, \text{K})_2\text{K}(\text{Zn}, \text{Li})_3[\text{Si}_{12}\text{O}_{30}]$ (Pautov *et al.* 1996, Sokolova & Pautov 1995), shibkovite, $(\text{Ca}, \text{Mn}, \text{Na})_2(\text{K}, \square)_2\text{KZn}_3[\text{Si}_{12}\text{O}_{30}]$ (Pautov *et al.* 1998, Sokolova *et al.* 1999), and berezanskite, $\text{Ti}_2(\square)_2\text{KLi}_3[\text{Si}_{12}\text{O}_{30}]$ (Pautov & Agakhanov 1997), and

(2) sugilite, $(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al})_2\text{Na}_2\text{KLi}_3[\text{Si}_{12}\text{O}_{30}]$ (milarite group; L.A. Pautov, unpubl. data) and zektzerite, $\text{NaLiZrSi}_6\text{O}_{15}$ (tuhualite group; Pautov & Ignatenko 1992).

The grains (0.2–2.0 mm) of darapiosite studied here come from a 10×30 cm quartz aggregate. They are pale violet and semitransparent, and were found in the central part of a dark bluish brown polymineralic aggregate (about 10×40 mm) that appears to be a partial replacement after darapiosite. The darapiosite-bearing aggregate is associated with minor crystals of aegirine, lamellar polyolithionite, fragments of microcline crystals, relics of reedmergnerite grains, and cavities resulting from the leaching of reedmergnerite.

EXPERIMENTAL

The chemical analysis of darapiosite (Table 1) was done by flame photometry for Li_2O and electron microprobe (EMPA) for the other elements (JXA–50A electron microprobe; 15 kV, 22 nA). The following standards were used: quartz, microcline USNM143968, gahnite USNM145883, zircon USNM117288–3, ja-

TABLE 1. CHEMICAL COMPOSITION OF DARAPIOSITE

	This paper*	Semenov <i>et al.</i> (1975)		This paper	Semenov <i>et al.</i> (1975)
SiO_2	63.19	63.65	Si	11.98	12.09
K_2O	5.63	5.14	K	1.36	1.24
FeO	1.96	1.67**	Fe^{2+}	0.31	0.26
MgO	0.12		Mg	0.03	
MnO	9.58	8.25	Mn^{2+}	1.54	1.33
CaO		0.57	Ca		0.12
ZnO	8.22	7.85	Zn	1.15	1.10
ZrO_2	3.28	5.00	Zr	0.30	0.46
Nb_2O_5		0.90	Nb		0.08
Na_2O	3.32	2.96	Na	1.22	1.09
Y_2O_3	2.26	0.96***	Y	0.23	0.10
Li_2O	2.01	1.74	Li	1.54	1.33
L.O.I.		0.58			
Total	99.57	99.27	Total	19.66	19.20

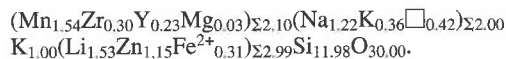
* Li_2O from flame photometry. L.O.I.: loss on ignition.

** Semenov *et al.* (1975) calculated the iron as Fe_2O_3 .

*** In Semenov *et al.* (1975), REE_2O_3 .

Compositions are calculated on the basis of 30 atoms of oxygen.

deite, Mn (metal), Y_2O_3 (USNM standards from Smithsonian Institution, Washington, D.C.). On the basis of 30 atoms of oxygen per formula unit, the following chemical formula is obtained [$\rho_{\text{meas}} = 2.92(3)$ g/cm³, microflotation]:



The IR spectrum of darapiosite (Fig. 1; Perkin Elmer Fourier spectrometer) shows stretching vibrations at 1117, 1041, 783 cm⁻¹ that are characteristic of the milarite-type minerals; no evidence of H_2O was observed. X-ray powder-diffraction data were obtained with a DRON–2 diffractometer ($\text{CuK}\alpha$ radiation, graphite monochromator) and indexed by taking into account the calculated powder-diffraction pattern (Table 2). Chemical, IR and diffraction data agree with those published for the holotype sample of darapiosite (Semenov *et al.* 1975).

X-ray single-crystal diffraction data were obtained with a SIEMENS P4 diffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation) from a crystal with dimensions $0.50 \times 0.32 \times 0.18$ mm. The following refined unit-cell parameters were obtained from 30 reflections ($10^\circ < \theta < 20^\circ$): a 10.262(2), c 14.307(1) Å, V 1305.0(3) Å³, space group $P6/mcc$. The integrated intensities of 6343 reflections with $-3 \leq h \leq 9$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$ were collected up to $2\theta = 60^\circ$ by the ω -scan method, with variable scan-speed as a function of reflection intensity. Using the program EQUIV (Prencipe 1998) for each subset of up to eight equivalent collected reflections (point group $6/mmm$), the standard deviation was evaluated and assigned to the average intensity. An empirical Ψ -scan absorption correction (North *et al.* 1968) was applied. The atomic coordinates of dusmat-

ovite (Sokolova & Pautov 1995) were used as the initial model of the structure. On the basis of 668 unique reflections, the crystal structure of darapiosite was refined anisotropically with SHELXL-93 (Sheldrick 1981) to $R = 0.032$ [$R = 0.031$ for 447 reflections with $|F_o| > 4\sigma(F_o)$] and a GooF of 1.23. A total of 44 parameters were refined, including an overall scale-factor and extinction as implemented in SHELXL-93. The scattering factors for neutral atoms were taken from Maslen *et al.* (1992); to account for cation substitutions, the occupancies of some sites were refined (Table 3). The refined numbers of electrons for the sites *A* (60.59), *B* (15.67), *C* (19.00) and *T2* (47.07) compared with those expected from the chemical analysis (56.98, 20.26, 19.00 and 47.31, normalized to integral occupancy of each site) show that, with respect to the material of the chemical analysis, the crystal used for the structural study must have a larger Zr content at the *A* site and either more Na or more vacancy at the *B* site. This crystal could not be analyzed by electron microprobe.

As in other members of the milarite group (Armbruster & Oberhänsli 1988, Hawthorne *et al.* 1991), the *B* site of darapiosite shows a strong anisotropic-displacement factor, with $U_{33} = 0.136 \text{ \AA}^2$ as compared with $U_{11} = U_{22} = 0.035 \text{ \AA}^2$, indicating some disorder along [001], which presumably is connected with the different type of cations at this site. A final difference elec-

tron-density synthesis showed no anomalies; the maximum and minimum residues were 0.48 and -1.05 electrons, respectively. A table of structure factors is deposited with the Depository of Unpublished Data, Canada Institute for Scientific and Technical Information, National Research Council, Ottawa, Ontario K1A 0S2.

RESULTS AND DISCUSSION

The crystal structure of darapiosite (Fig. 2, Table 4) shows the double-ring features typical of milarite-group minerals, which have the general formula ${}^{\text{VI}}\text{A}_2{}^{\text{IX}}\text{B}_2{}^{\text{XII}}\text{C}^{\text{XVIII}}\text{D}^{\text{IV}}(\text{T2})_3{}^{\text{IV}}(\text{T1})_{12}\text{O}_{30}$ (Forbes *et al.* 1972). From Figure 2, it is clear that the *T2* tetrahedra and the *A* octahedra are on the same (001) plane; these polyhedra connect the double rings along [001] and sandwich the nine-coordinated *B* cations, which surround the same rings. The twelve-coordinated *C* cations are located on the axis of the channels, which cross the structure along [001]. The compositions of the *A*, *B* and *T2* sites are shown in Table 5; *C* is fully occupied by K, and *D* is empty as in most minerals of the group (Hawthorne *et*

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR DARAPIOSITE

<i>hkl</i>	Semenov <i>et al.</i> (1975)		This paper*		Calculated	
	I_{obs}	d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{calc}	d_{calc} (Å)
100			26	8.90	18	8.89
002	6	7.09	100	7.15	66	7.15
102	3.5	5.57	45	5.58	24	5.57
110	3	5.02			3	5.13
200	4	4.43	55	4.44	44	4.44
112	5	4.13	70	4.16	63	4.17
202	4	3.75	52	3.776	53	3.774
004	2.5	3.55	30	3.570	13	3.577
104			48	3.314	33	3.318
211	10	3.26	80	3.270	100	3.270
212	1.5	3.04	25	3.043	14	3.040
300	6.5	2.93	96	2.931	14	2.962
114			22	2.902	99	2.934
204	4.5	2.76	48	2.783	44	2.786
213			22	2.746	15	2.746
220	5.5	2.56	33	2.564	56	2.565
311	2	2.41	18	2.423	8	2.429
222					12	2.415
304	2	2.271	22	2.277	12	2.281
313	1.5	2.182	18	2.186	11	2.190
224	2	2.082	17	2.082	19	2.085
320	2.5	2.024	25	2.028	8	2.039
314					27	2.029
410	2	1.928	18	1.918	13	1.939
411					11	1.922
412	3	1.863	22	1.867	8	1.872
315					15	1.867
306					7	1.857
008	2.5	1.783	25	1.785	16	1.788
500					16	1.777
226	3.5	1.742	30	1.743	29	1.746
414	1.5	1.704			10	1.705
511	2	1.583			9	1.586
334	2	1.541			16	1.543
228	2.5	1.466	22	1.466	22	1.467
602	2	1.450	15	1.448	11	1.450
520	2.5	1.421	15	1.419	17	1.423

* Quartz as an internal standard.

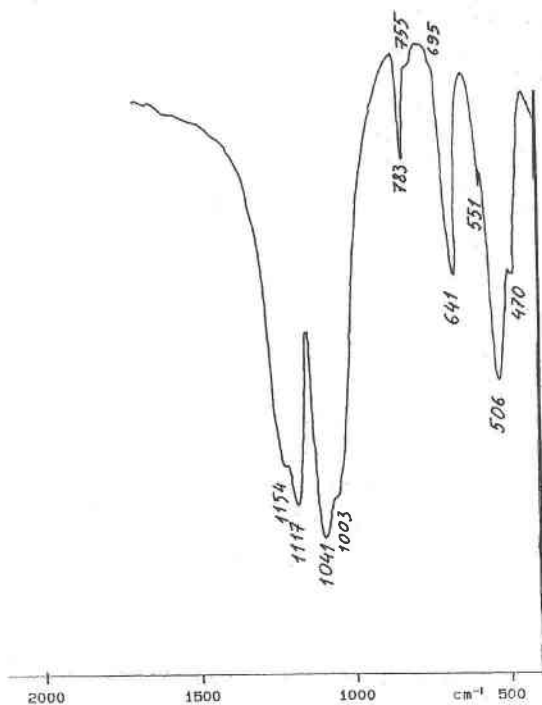


FIG. 1. The infrared absorption spectrum of darapiosite.

TABLE 3. ATOM COORDINATES, EQUIVALENT DISPLACEMENTS (\AA^2) AND NUMBER OF ELECTRONS EI AT THE SITES A, B, C AND T2 FOR THE DARAPIOSITE STRUCTURE

A	x	1/3	T2	x	0
	y	2/3		y	1/2
	z	1/4		z	1/4
	U_{eq}	0.0117(2)		U_{eq}	0.0122(3)
	EI	60.59(1)		EI	47.07(1)
B	x	1/3	O1	x	0.1250(4)
	y	2/3		y	0.3857(4)
	z	0		z	0
	U_{eq}	0.069(2)		U_{eq}	0.0283(7)
	EI	15.68(1)			
C	x	0	O2	x	0.2142(2)
	y	0		y	0.2743(2)
	z	1/4		z	0.1355(2)
	U_{eq}	0.0236(4)		U_{eq}	0.0222(5)
	EI	19.00(5)			
T1	x	0.10900(8)	O3	x	0.1530(2)
	y	0.34665(8)		y	0.4946(2)
	z	0.11042(5)		z	0.1687(1)
	U_{eq}	0.0122(2)		U_{eq}	0.0176(4)

According to the formula $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$,

al. 1991). Darapioisite is close to dusmatovite in chemical composition (Table 5). Both minerals have Mn^{2+} as dominant cation at the A site and differ mainly in the major cation at the T2 and B sites. Darapioisite is characterized by Li and Na dominant at T2 and B, respectively; Zn and \square (vacancy) are dominant at T2 and B in dusmatovite.

In the milarite group, according to Winter *et al.* (1995) the T1–O2–T1 angle within a six-membered ring

TABLE 4. SELECTED INTERATOMIC DISTANCES (\AA) AND ANGLES ($^\circ$) IN THE STRUCTURE OF DARAPIOSITE

A–O3	$\times 6$	2.151(2)	T2–O3	$\times 4$	1.976(2)
O3–O3a	$\times 3$	2.869(4)	O3–O3a	$\times 2$	2.869(4)
O3–O3b	$\times 3$	3.025(4)	O3–O3e	$\times 2$	3.196(4)
O3–O3c	$\times 6$	3.134(3)	O3–O3f	$\times 2$	3.578(4)
Average		3.099	Average		3.214
O3–A–O3a	$\times 3$	83.6(1)	O3–T2–O3a	$\times 2$	93.1(1)
O3–A–O3b	$\times 3$	89.4(1)	O3–T2–O3e	$\times 2$	107.9(1)
O3–A–O3c	$\times 6$	93.53(7)	O–T2–O3f	$\times 2$	129.7(1)
Average		90.0	Average		110.2
B–O1	$\times 3$	2.592(4)	C–O2	$\times 12$	3.042(2)
B–O3	$\times 6$	3.017(2)			
Average		2.875			
T1–O1		1.618(1)			
T1–O2		1.621(2)			
T1–O2d		1.627(2)			
T1–O3		1.588(2)			
Average		1.614			
O1–O2		2.636(3)	O1–T1–O2		108.6(2)
O1–O2d		2.668(3)	O1–T1–O2d		110.9(2)
O1–O3		2.615(2)	O1–T1–O3		109.4(2)
O2–O2d		2.562(2)	O2–T1–O2d		104.2(2)
O2–O3		2.675(3)	O2–T1–O3		112.6(1)
O2d–O3		2.645(3)	O2d–T1–O3		111.0(1)
Average		2.634	Average		109.5

$a = x, 1 - y + x, 1/2 - z; b = y - x, y, 1/2 - z; c = 1 - y, 1 - y + x, z;$
 $d = x - y, x, z; e = -x, 1 - y, z; f = -x, y - x, 1/2 - z.$

and the T1–O1–T1 angle between two stacked rings are ideally constrained by the equation $Ti-O2-T1 = 227.44 - 0.4784 \times T1-O1-T2$. In darapioisite, with $Ti-O2-T1$ equal to 153.24° and $T1-O1-T1$ equal to 155.12° , that

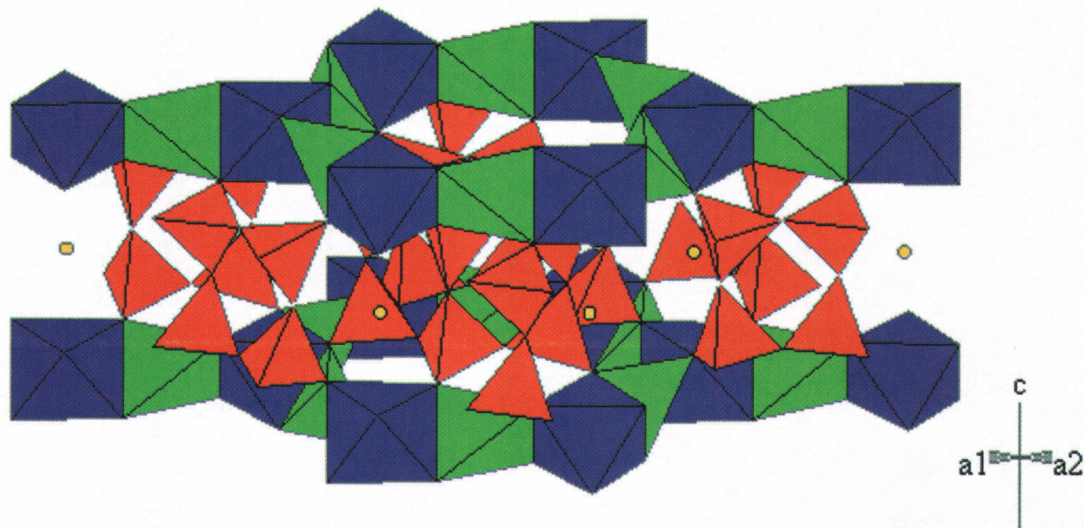


Fig. 2. Perspective view of the crystal structure of darapioisite along $[110]$. Crystallographically equivalent polyhedra have the same color; yellow circles represent the B sites.

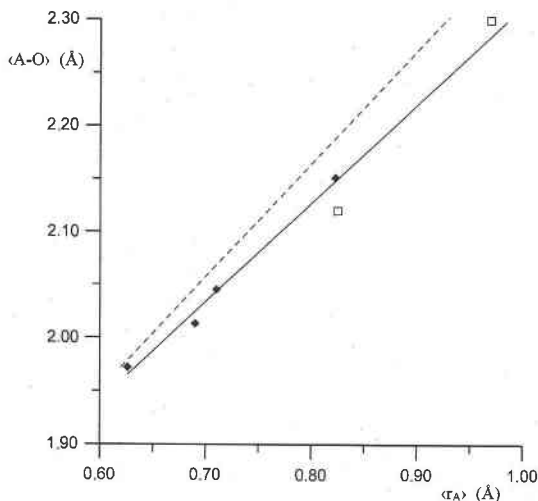


FIG. 3. $\langle A-O \rangle$ versus the aggregate radius $\langle r_A \rangle$ of the octahedrally coordinated cation (Table 5; Shannon 1976) of the constituent cation at the A site, calculated according to the compositions in Table 5. The regression (full line) is through the filled squares, which represent (from the bottom) sugilite, brannockite, sogdianite and darapiosite; the broken line is that given in Figure 13 of Hawthorne *et al.* (1991) for other members of the milarite group. Open squares represent (from the bottom) dusmatovite and shibkovite.

equation is closely satisfied and consequently (Winter *et al.* 1995), the T1–O3 bond (1.588 Å, Table 4) is short.

Since publication of the paper by Hawthorne *et al.* (1991) on the crystal chemistry of the milarite group, some new crystal structures of Li-bearing species belonging to the group have been refined (Tables 5, 6). Comparison of the data given in Table 5 shows that darapiosite has the largest $\langle T2-O \rangle$ distance and cell parameters. This feature is due to the presence at the T2 site of Fe^{2+} , which is larger (${}^{IV}r = 0.63$ Å; Shannon 1976) than Li (${}^{IV}r = 0.59$ Å) and Zn^{2+} (${}^{IV}r = 0.60$ Å). Moreover, Armbruster & Oberhänsli (1988) showed that in the milarite group, a increases with the length of the edge shared between the T2 tetrahedron and the A octahedron, and c increases with the size of the C and T2 sites.

Hawthorne *et al.* (1991) showed that the $\langle A-O \rangle$ distance is a linear function ($\langle A-O \rangle = 1.311 + 1.066 \langle r_A \rangle$) of the radius $\langle r_A \rangle$ weighted according to the cation composition of the A site. However, brannockite and sogdianite [which has recently been refined by Cooper *et al.* (1999)] do not obey this correlation (see their Fig. 13) in such a way that the correlation appeared broken into two segments. Addition of data from the recently refined structures (Table 6) shows that a linear correlation $\langle A-O \rangle = 1.38(5) + 0.93(7) \langle r_A \rangle$ holds (Fig. 3) for sugilite, brannockite, sogdianite and darapiosite,

TABLE 5. CHEMICAL COMPOSITION OF SITES, ABSOLUTE DIFFERENCE $|\Delta Ch|$ BETWEEN THE CHARGE AT A AND T2, AND AGGREGATE RADIUS $\langle r_A \rangle$ IN THE LI- AND ZN-BEARING MINERALS OF THE MILARITE GROUP

	A site	B site	T2 site	$ \Delta Ch $	$\langle r_A \rangle$
Sugilite ¹	$Fe^{3+}_{1.66} Al^{2+}_{0.34}$	$\square_{0.04} Nb_{1.96}$	Li ₃	2.00	0.63
Brannockite ¹	Sn ₂	$\square_{2.0}$	Li ₃	3.00	0.69
Sogdianite ²	$Zr_{0.90} Fe^{3+}_{0.56}$ $Ti_{0.28} Fe^{2+}_{0.25}$	$\square_{1.0} Na_{0.90}$ K _{0.10}	$Li_{2.85} Al_{0.15}$	2.37	0.73
Dusmatovite ³	$Mn_{1.52} Zr_{0.24}$ Y _{0.24}	$\square_{1.0} Na_{0.64}$ K _{0.36}	$Zn_{2.28} Li_{0.72}$	0.60	0.83
Darapiosite ⁴	$Mn_{1.47} Zr_{0.28}$ $Y_{0.22} Mg_{0.03}$	$Nb_{1.22} K_{0.36}$ $\square_{0.42}$	$Li_{1.54} Zn_{1.13}$ $Fe^{2+}_{0.31}$	0.90	0.82
Shibkovite ⁵	$Ca_{1.26} Mn_{0.40}$ $Nb_{0.34}$	$\square_{0.74} K_{1.26}$	Zn ₃	0.17	0.97

¹ Armbruster & Oberhänsli (1988), ² Kabalov *et al.* (1993), ³ Sokolova & Pautov (1995), ⁴ this paper, ⁵ Sokolova *et al.* (1999). The occupancy of the sites are normalized to integers.

TABLE 6. UNIT-CELL PARAMETERS (Å) AND SELECTED INTERATOMIC DISTANCES (Å) IN LI- AND ZN-BEARING MINERALS OF THE MILARITE GROUP

	a	c	A–O3	T2–O3	O3–O3a	T1–O3	C–O2
Sugilite	10.009	14.006	1.972	1.970	2.681	1.577	2.994
Brannockite	10.002	14.263	2.013	1.922	2.672	1.594	3.055
Sogdianite	10.037	14.199	2.045	1.910	2.689	1.577	3.012
Dusmatovite	10.218	14.292	2.120	1.971	2.832	1.583	3.044
Darapiosite	10.262	14.307	2.151	1.976	2.869	1.588	3.042
Shibkovite	10.502	14.184	2.300	1.959	2.973	1.586	3.009

i.e., for those members of the milarite group where Li is dominant at T2 (Table 5). Thus, the reason for the split of the linear correlation, as reported in Figure 13 of Hawthorne *et al.* (1991), must be ascribed to a dependence of $\langle A-O \rangle$ on both $\langle r_A \rangle$ and the Li content of the T2 site (Table 6). The point representing dusmatovite, in which Zn is the major cation at T2, does not fit properly, either our correlation or that of Hawthorne *et al.* (1991) (Fig. 3). Instead, shibkovite, $(Ca, Mn, Na)_2(K, \square)_2 KZn_3[Si_{12}O_{30}]$, a new mineral of the milarite group recently discovered (Sokolova *et al.* 1999) that contains only Zn at T2 (Tables 5, 6), fits both correlations. Multiple-regression analysis including the size and the charge of the average cations at the A and T2 sites (Table 5) shows that $\langle A-O \rangle$ depends directly on both $\langle r_A \rangle$ and the absolute difference $|\Delta Ch|$ between the charge at T2 and A. As dusmatovite and darapiosite have close values of $\langle r_A \rangle$, the anomalous behavior in the $\langle A-O \rangle$ versus $\langle r_A \rangle$ correlation (Fig. 3) may well be ascribed to the small value of $|\Delta Ch|$ in dusmatovite.

CONCLUSIONS

The crystal structure of darapiosite, together with recent data published for Li-bearing minerals of the milarite group, allow us to explain crystal-chemical features connected with the presence of Li at T2 that were not clear from earlier work. The occurrence of Zn at the T2 site further modifies relations between this site and other parts of the structure.

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