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THE CRYSTAL CHEMISTRY OF Li-BEARING MINERALS WITH THE MILARITE-TYPE STRUCTURE: THE CRYSTAL STRUCTURE OF END-MEMBER SOGDIANITE

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ABSTRACT

The crystal structure of end-member sogdianite from the Dara-i-Pioz alkaline massif, northern Tajikistan, *a* 10.1240(3), *c* 14.3198(5) Å, *V* 1271.1(1) Å^3, space group *P*6/*mcc*, Z = 2, has been refined to an *R* index of 2.0% using 576 observed ($|F_o| > 4\sigma F$) reflections collected with single-crystal diffractometer with Mo*K*α X-radiation. Electron-microprobe analysis gives a composition $(Zr_{1.98}\ Hf_{002})_{\Sigma 2.00}\ (K_{0.99}\ Na_{0.01})_{\Sigma 1.00}\ Li_{2.97}\ Si_{12.01}\ O_{30}$. The sogdianite end-member has the typical structure of the double-ring silicates of the milarite structure-type: the *A* octahedron and *T*(2) tetrahedron are completely occupied by Zr and Li, and tetravalent Zr at the *A* site induces the lack of Na at the *B* site. The simplified chemical formula $Zr_2\ K\ Li_3\ Si_{12}\ O_{30}$ corresponds to the ideal end-member formula of sogdianite $(Zr,Ti^{4+},Fe^{3+},Al)_2\ (\square,Na)_2\ K\ [Li_3Si_{12}O_{30}]$ with Zr dominant at the *A* site and $\square$ (vacancy) dominant at the *B* site: $Zr_2\ \square_2\ K\ [Li_3\ Si_{12}\ O_{30}]$.

Keywords: sogdianite, milarite-type structure, end-member, crystal chemistry.

SOMMAIRE

Nous avons affiné la structure cristalline d'un échantillon de sogdianite dont la composition est celle du pôle, provenant du complexe alcalin de Dara-i-Pioz, dans la partie nord du Tajikistan, *a* 10.1240(3), *c* 14.3198(5) Å, *V* 1271.1(1) Å^3, groupe spatial *P*6/*mcc*, *Z* = 2, jusqu'à un résidu *R* de 2.0% en utilisant 576 réflexions observées ($|F_o| > 4\sigma F$) prélevées sur cristal unique au moyen d'un diffractomètre avec rayonnement Mo*K*α. Une analyse à la microsonde électronique a donné $(Zr_{1.98}Hf_{002})_{\Sigma 2.00}\ (K_{0.99}\ Na_{0.01})_{\Sigma 1.00}\ Li_{2.97}\ Si_{12.01}\ O_{30}$. La sogdianite pure possède la structure typique à anneaux doubles de tétraèdres silicatés des membres du groupe de la milarite. Les octaèdres *A* et les tétraèdres *T*(2) sont complètement remplis par le Zr et le Li; la présence du Zr tétravalent dans le site *A* est la cause de l'absence de Na au site *B*. La formule chimique simplifiée, $Zr_2\ K\ Li_3\ Si_{12}\ O_{30}$, correspond au pôle idéal de la sogdianite, plus généralement représentée par $(Zr,Ti^{4+},Fe^{3+},Al)_2\ (\square,Na)_2\ K\ [Li_3Si_{12}O_{30}]$, avec Zr dominant au site *A* et une lacune ($\square$) dominante au site *B*: $Zr_2\ \square_2\ K\ [Li_3\ Si_{12}\ O_{30}]$.

Mots-clés: sogdianite, structure du type de la milarite, pôle, cristallochimie.

INTRODUCTION

Sogdianite from the alkaline massif of Dara-i-Pioz, northern Tajikistan, was described by Dusmatov *et al.* (1968) as a new mineral with the formula $(K,Na)_2\ Li_2\ (Li,Fe,Al,Ti)_{1.8}\ (Zr,Ti)\ [Si_{12}O_{30}]$. Its structure was solved by Bakakin *et al.* (1975) and then refined both from powder X-ray data (Kabalov *et al.* 1994) and from single-crystal X-ray data (Cooper *et al.* 1999). All studies of the crystal structure of sogdianite confirmed its affinity to the milarite structure-type with a general formula of $^{[6]}A_2\ ^{[9]}B_2\ ^{[12]}C\ ^{[18]}D\ ^{[4]}T(2)_3\ ^{[4]}T(1)_{12}\ O_{30}$ (Forbes *et al.* 1972). The *T*(2) tetrahedra and *A* octahedra connect the $[T_{12}O_{30}]$ double-rings along the *c* axis. The [12]-coordinated *C* cations are located on the axis of the channels that extend along [001]. In contrast to the sogdianite formula $K\ (Zr,Fe^{3+},Ti,Fe^{2+})_2\ (Li,Al,\square)_3\ [Si_{12}O_{30}]\ (Na,K)$ proposed by Bakakin *et al.* (1975), Cooper *et al.* (1999) wrote the formula as $(Zr,Ti^{4+},Fe^{3+},Al)_2\ (\square,Na)_2\ K\ [Li_3Si_{12}O_{30}]$ ($\square$: vacancy) and speculated on a possible formula of the ideal end-member of the sogdianite–sugilite $(Fe^{3+}{}_2\ Na_2\ K\ [Li_3\ Si_{12}$

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O_{30}]) solid-solution series as $Zr_2 \square_2$ K [Li_3 Si_{12} O_{30}], the latter having Zr dominant at the *A* site and □ dominant at the *B* site.

At the same time, Na-free sogdianite was found at the Dara-i-Pioz moraine, and here we report crystallographic characterization of the sogdianite end-member of the sogdianite–sugilite solid-solution series: $Zr_2 \square_2$ K [Li_3 Si_{12} O_{30}].

OCCURRENCE

End-member sogdianite was found in a quartz–aegirine aggregate in the moraine of the Dara-i-Pioz glacier (southern slope of the Alai mountain ridge, Garm district, northern Tajikistan). The Dara-i-Pioz alkaline massif is confined to the intersection of the Alai, Gissar, Zeravshan and Turkestan mountain ridges. The glacial valley cuts the upper Dara-i-Pioz massif, which is related to the late Permian – early Triassic Alai intrusive complex. The external part of the complex consists of fine-grained subalkaline biotite granites and represents a second-stage intrusion of the Turkestan complex; its central part consists of alkaline rocks, *i.e.*, syenites and foyaites of the Alai complex, crossed by veins of syenite aplites, pegmatites, quartz and carbonatites.

Usually, the sogdianite end-member occurs in multimineral pseudomorphs after eudialyte. These pseudomorphs also contain bazirite, $BaZrSi_3O_9$ (Pautov & Khvorov 1998), calcite and relics of eudialyte, and occur in a massive quartz–aegirine aggregate with a small amount of titanite and turkestanite. The sogdianite end-member crystallizes as short prisms (0.3 × 0.5 mm; Fig. 1) with numerous inclusions of bazirite. The crystals of sogdianite are colorless (in contrast to the pink crystals of sogdianite characterized by Cooper *et al.* 1999) or white because of inclusions of bazirite, semitransparent, and with a vitreous luster. The forms {100} and {001} are prevalent. In ultraviolet light, the mineral fluoresces blue. In thin section, the sogdianite end-member is transparent and colorless.

ELECTRON-MICROPROBE ANALYSIS

Chemical analysis of the sogdianite end-member (Table 1) was done by atomic absorption (Li, Na and K) and electron-microprobe analysis (for other elements; JCXA–733 electron microprobe; 20 kV, 21 nA). Standards were as follows: osumilite USNM 110607 for Si, K, Fe; zircon USNM117288–3 for Zr, Hf; augite USNM122142 for Na (USNM standards from the Smithsonian Museum, Washington, D.C.). In spite of careful preparation of samples, it was very difficult to get pure grains of sogdianite without any trace of bazirite; the presence of bazirite inclusions resulted in a slightly underestimated value of the Li content. On the basis of 30 oxygen atoms *pfu* (per formula unit), the following chemical formula for the sogdianite end-member was obtained: $(Zr_{1.98}\ Hf_{002})_{\Sigma 2.00}$ $(K_{0.99}\ Na_{0.01})_{\Sigma 1.00}$ $Li_{2.97}$ $Si_{12.01}$ O_{30}, which approximates very closely to Zr_2 K Li_3 Si_{12} O_{30}.

COLLECTION OF X-RAY DATA AND CRYSTAL-STRUCTURE REFINEMENT

Single-crystal X-ray-diffraction data for the sogdianite end-member were collected with a Siemens

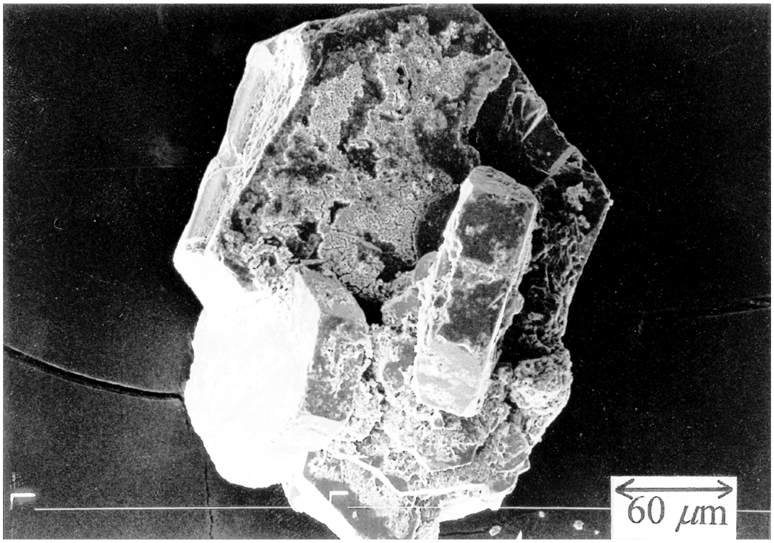

FIG. 1. Image of crystals of end-member sogdianite, as obtained by scanning electron microscopy. The scale bar represents 60 μm.

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND FORMULA UNIT (*apfu*) OF END-MEMBER SOGDIANITE

	End-member sogdianite	(1)**	(2)**		End-member sogdianite	(1)**	(2)**
SiO_2	68.15	68.06	68.83	Si	12.01	12	11.93
Al_2O_3	n.d.*	–	1.04				
TiO_2	n.d.	–	2.88	K	0.99	1	1.07
Fe_2O_3	–	–	4.61	Ba			0.02
FeO	0.02	–	1.22				
HfO_2	0.34	–	–	Fe^{3+}			0.60
ZrO_2	23.09	23.26	9.78	Fe^{2+}	0.00		0.18
BaO	n.d.	–	0.32	Hf	0.02		
K_2O	4.42	4.45	4.84	Zr	1.98	2	0.83
Na_2O	0.02	–	2.81	Al			0.21
Li_2O	4.19	4.23	3.73	Ti			0.38
Total	100.23	100.00	100.06	Na	0.01		0.94
				Li	2.97	3	2.60
				O	30.00	30	30.00

* not detected
**(1) calculated based on the ideal formula $K Li_3 Zr_2 [Si_{12}O_{30}]$;
(2) taken from Dusmatov *et al.* (1968).

TABLE 2. MISCELLANEOUS CRYSTAL-STRUCTURE REFINEMENT DATA FOR END-MEMBER SOGDIANITE

a (Å)	10.1240(3)
c (Å)	14.3198(5)
V (Å³)	1271.1(1)
Space group	*P6/mcc*
Z	2
Absorption coefficient (mm⁻¹)	1.68
D(meas) *	2.78(2) g/cm³
F(000)	1032
Crystal size (mm)	0.03 x 0.11 x 0.15
Radiation	Mo*K*α
2θ range for data collection (E)	59.82
R(int) (%)	3.2
Reflections collected $F_o > 4\sigma F$	11927 10453
Unique reflections $F_o > 4\sigma F$	653 576
Refinement method	Full-matrix least-squares on F^2; fixed weights proportional to $1/\sigma(F_o^2)$
Goodness of fit on F^2	1.100
Final *R* index [$F_o > 4\sigma F$]	$R_1 = 2.00$
R index(all data)	$R_1 = 2.37$ $wR_2 = 5.58$ GooF = 1.100

* measured by microflotation.

*P*4 diffractometer fitted with a CCD detector, using Mo*K*α X-radiation and an irregular fragment with dimensions 0.03 × 0.11 × 0.15 mm. The integrated intensities of 11981 reflections with $14 \le h \le 14$, $14 \le k \le 14$, 20 $1 \le l \le 20$ were collected up to 2θ = 59.90° using 30 s per frame. The refined unit-cell parameters (Table 2) were obtained from 6150 reflections (I > 10σI). An empirical absorption-correction (SADABS, Sheldrick 1996) was applied.

The atomic coordinates of sogdianite (Cooper *et al.* 1999) were used as the initial structure-model. On the basis of 576 unique observed reflections, the crystal structure of sogdianite was refined with SHELXL–93 (Sheldrick 1993) to an *R* of 2.0% and a GooF of 1.10 for a total of 42 refined parameters. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). Refined site-occupancies for the *A* and *T*(2) sites indicate the presence of Zr and Li. A final difference electron-density map shows no maximum at the *B* site, thus confirming the vacancy at this site. Final atom parameters are given in Table 3, and selected interatomic distances are given in Table 4. Final observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CRYSTAL STRUCTURE

Sogdianite is a member of the milarite group (Černý *et al.* 1980, Hawthorne *et al.* 1991). In the basic structure of these minerals, pairs of opposing $[Si_6O_{18}]$ rings of tetrahedra meld to form $[Si_{12}O_{30}]$ cages that stack to form columns parallel to the *c* axis (Fig. 2). The columns are arranged at the vertices of a 3^6 net and are linked both horizontally and vertically by additional tetrahedra [formally labeled *T*(2) in this structure type]. Additional linkage is provided by octahedrally coordinated cations that are labeled *A*. Viewed down the *c* axis, the structure is virtually identical to that of beryl (Fig. 2a). Viewed along [100] (Fig. 2b), the $[Si_{12}O_{30}]$

TABLE 3. FINAL ATOMIC PARAMETERS FOR END-MEMBER SOGDIANITE

	x	y	*z*	U_{eq} *	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A	1/3	2/3	1/4	61(1)	59(2)	59(2)	67(2)	0	0	29(1)
C	0	0	1/4	217(3)	207(4)	207(4)	236(7)	0	0	104(2)
T(1)	0.11184(5)	0.35135(5)	0.10941(3)	73(1)	68(2)	80(2)	71(2)	–10(2)	–5(2)	37(2)
T(2)	0	1/2	1/4	141(12)	74(26)	146(21)	178(28)	0	0	37(13)
O(1)	0.1246(2)	0.3911(2)	0	164(4)	232(10)	197(10)	61(8)	0	0	105(8)
O(2)	0.2179(1)	0.2779(2)	0.13483(8)	138(3)	134(6)	164(7)	164(7)	–3(5)	–5(5)	109(5)
O(3)	0.1565(1)	0.4983(1)	0.17173(8)	101(3)	99(5)	102(5)	97(6)	–28(5)	–12(4)	46(5)

U_{ij} x 10^4

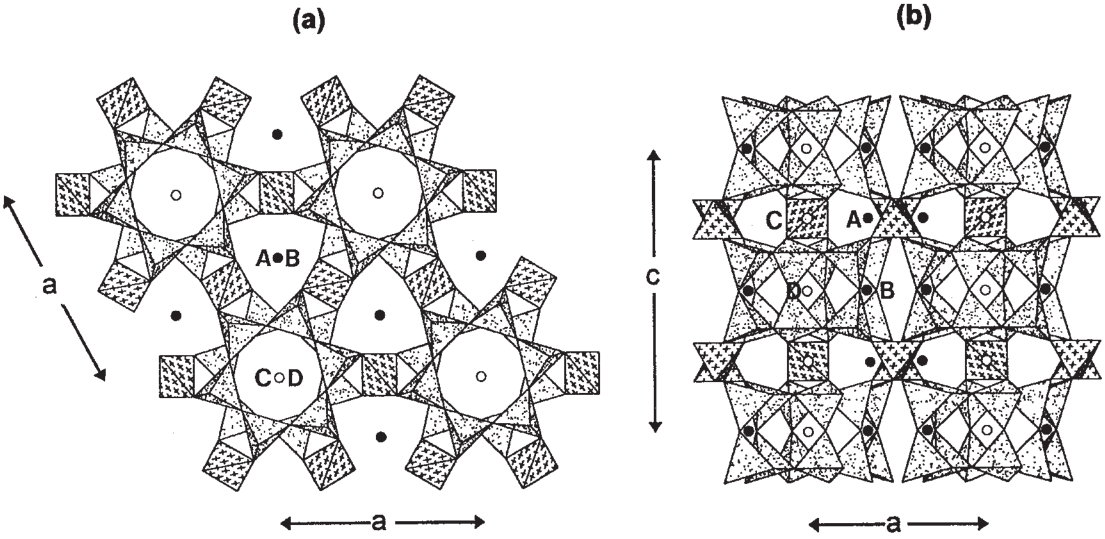

FIG. 2. The crystal structure of the milarite-group minerals: (a) projected onto (001); (b) projected along [100].

cages are apparent. The *B* site occurs on the six-fold axis between the [$Si_{12}O_{30}$] cages, and is [9]-coordinated. The *C* site occurs on the six-fold axis within the [$Si_{12}O_{30}$] cage, and is [12]-coordinated. The *D*-site occurs on the three-fold axis at the same level as the [$Si_{12}O_{30}$] cages, and is [18]-coordinated. The occupancies of the various sites are given in Table 5.

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN END-MEMBER SOGDIANITE

A–O(3)	x6	2.077(1)	*T*(2)–O(3)	x4	1.947(1)
O(3)–O(3)*a*	x3	2.764(2)	O(3)–O(3)*a*	x2	2.764(2)
O(3)–O(3)*b*	x3	2.923(2)	O(3)–O(3)*e*	x2	3.185(2)
O(3)–O(3)*c*	x6	3.029(2)	O(3)–O(3)*f*	x2	3.543(2)
<O–O>*A*		2.905	<O–O>*T*(2)		3.164
O(3)–*A*–O(3)*a*	x3	83.42(6)	O(3)–*T*(2)–O(3)*a*	x2	90.43(7)
O(3)–*A*–O(3)*b*	x3	89.45(7)	O(3)–*T*(2)–O(3)*e*	x2	109.72(7)
O(3)–*A*–O(3)*c*	x6	93.63(4)	O(3)–*T*(2)–O(3)*f*	x2	130.91(7)
<O–*A*–O>		90.03	<O–*T*(2)–O>		110.35
C–O(2)	x12	3.049(1)			
T(1)–O(1)		1.607(1)	O(1)–*T*(1)–O(2)		110.14(8)
T(1)–O(2)		1.624(1)	O(1)–*T*(1)–O(2)*d*		110.23(9)
T(1)–O(2)*d*		1.623(1)	O(1)–*T*(1)–O(3)		111.25(9)
T(1)–O(3)		1.595(1)	O(2)–*T*(1)–O2*d*		104.35(9)
<*T*(1)–O>		1.612	O(2)–*T*(1)–O(3)		110.99(7)
			O(2)d–*T*(1)–O(3)		109.68(6)
O(1)–O(2)		2.649(2)	<O–*T*(1)–O>		109.44
O(1)–O(2)*d*		2.649(2)			
O(1)–O(3)		2.642(2)			
O(2)–O(2)*d*		2.564(1)			
O(2)–O(3)		2.653(2)			
O(2)d–O(3)		2.631(2)			
<O–O>*T*(1)		2.631			

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.

In the crystal structure of end-member sogdianite, four sites, *A*, *C*, *T*(1), and *T*(2), are completely occupied by Zr, K, Si and Li, respectively; the *B* and *D* sites are vacant. End-member sogdianite differs from sogdianite as described by Dusmatov *et al.* (1968) by the absence of Na at the *B* site and Fe^{3+}, Ti^{4+} and Fe^{2+} at the *A* site.

In the end-member sogdianite structure, the <*T*(1)–O> distance, 1.612 Å (Table 4), is the same as in the sample of sogdianite refined by Cooper *et al.* (1999). This is the only cation–anion distance that is the same in each structure. The *C* site is occupied by K, and the *C*–O(2) distance is 3.049 Å, compared to 3.033 Å (Cooper *et al.* 1999).

The *A* site is occupied by Zr ($^{[6]}r$ = 0.72 Å; radii from Shannon 1976), and the *A*–O(3) distance is 2.077 Å compared to 2.019 Å in sogdianite, where the *A* site is partly occupied by the smaller cations Fe^{3+} ($^{[6]}r$ = 0.645 Å), Ti ($^{[6]}r$ = 0.605 Å), and Al ($^{[6]}r$ = 0.535 Å) (Table 6); the hard-sphere model *A*–O(3) distance, 2.080 Å, is in

TABLE 5. SITE OCCUPANCIES IN THE MILARITE-GROUP MINERALS

Site	Equipoint	C.N.	Occupancy
T(1)	24m	4	Si, Al
T(2)	6f	4	Li, Be, B, Mg, Al, Si, Mn^{2+}, Zn
A	4c	6	Al, Fe^{3+}, Sn^{4+}, Mg, Zr, Fe^{2+}, Ca, Na, Y, REE
B	4d	9	Na, H_2O, □, Ca?, K
C	2a	12	K, Na, Ba, □, Ca?
D	2b	18	□, ?

TABLE 6. ASSIGNED SITE-POPULATIONS (*apfu*) AND CALCULATED AND OBSERVED DISTANCES FOR Li- AND Zn-BEARING MINERALS OF THE MILARITE-TYPE STRUCTURE

Mineral	*A* site			*B* site	*T*(2) site		
	Site-population	$<A\text{–O}>_{calc}$ *	$<A\text{–O}>_{obs}$	Site-population	Site-population	$<T(2)\text{–O}>_{calc}$ *	$<T(2)\text{–O}>_{obs}$
Sugilite[1]	$Fe^{3+}_{1.66}\,Al^{3+}_{0.34}$	1.970	1.972	$\square_{1.02}\,Na_{0.98}$	Li_3	1.950	1.970
Brannockite[1]	Sn^{4+}_2	2.050	2.013	$\square_{2.0}$	Li_3	1.950	1.922
Sogdianite [2]	$Zr_{0.76}\,Fe^{3+}_{0.73}\,Ti_{0.38}\,Al_{0.13}$	2.030	2.019	$\square_{1.15}\,Na_{0.85}$	Li_3	1.950	1.957
Sogdianite [3]	Zr_2	2.080	2.077	$\square_{2.0}$	Li_3	1.950	1.947
Dusmatovite[4]	$Mn^{2+}_{1.52}\,Zr_{0.24}\,Y_{0.24}$	2.180	2.120	$\square_{1.0}\,Na_{0.64}\,K_{0.36}$	$Zn_{2.28}\,Li_{0.72}$	1.960	1.971
Darapiosite[5]	$Mn^{2+}_{1.47}\,Zr_{0.28}\,Y_{0.22}\,Mg_{0.03}$	2.180	2.151	$Na_{1.22}\,K_{0.36}\,\square_{0.42}$	$Li_{1.54}\,Zn_{1.15}\,Fe^{2+}_{0.31}$	1.950	1.976
Shibkovite[6]	$Ca_{1.26}\,Mn^{2+}_{0.40}\,Na_{0.34}$	2.330	2.300	$\square_{0.74}\,K_{1.26}$	Zn_3	1.960	1.959

*Calculated by summing the constituent ionic radii; values from Shannon (1976); O = O(3);
[1] Armbruster & Oberhänsli (1988); [2] Cooper et *al*. (1999); [3] This paper; [4] Sokolova & Pautov (1995); [5] Ferraris et *al*. (1999);
[6] Sokolova et *al*. (1999).

TABLE 7. BOND-VALENCE (*vu*) CALCULATIONS AROUND O(3) FOR Li- AND Zn-BEARING MINERALS OF THE THE MILARITE-TYPE STRUCTURE

Mineral	*A**	*B***	*T*(1)**	*T*(2)*	ΣO(3)
Sugilite	0.50	0.08	1.14	0.25	1.97
Brannockite	0.67	0	1.14	0.25	2.06
Sogdianite	0.60	0.03	1.10	0.25	1.98
Sogdianite	0.67	0	1.08	0.25	2.00
Dusmatovite	0.39	0.03	1.12	0.44	1.96
Darapiosite	0.40	0.04	1.10	0.37	1.91
Shibkovite	0.31	0.05	1.11	0.50	1.97

* Pauling's second rule was used to calculate the bond valence from the *A* and *T*(2) cations around O(3);
** bond-valence curves for Na and Si from Brown & Altermatt (1985) were used.

close agreement with the observed value of 2.077 Å. Hawthorne *et al.* (1991) showed that there is a close correlation between <*A*–O> and the constituent-cation radius of the *A*-group cations: a linear model with a correlation coefficient of 0.983 and the form <*A*–O> = 1.311 + 1.066 $<r_A>$ was reported for the milarite-group minerals ($<r_A>$ = mean radius of the constituent *A* cations). Hawthorne *et al.* (1991) also reported the possible existence of two distinct correlations. Additional data, recently obtained for darapiosite, dusmatovite $(Mn,Zr,Y)_2\,(\square,Na,K)_2\,K\,(Zn,Li)_3\,[Si_{12}O_{30}]$ (Sokolova & Pautov 1995, Pautov *et al.* 1996) and shibkovite $(Ca,Mn,Na)_2\,(K)_2\,K\,Zn_3\,[Si_{12}O_{30}]$ (Pautov *et al.* 1998, Sokolova *et al.* 1999) support the existence of two distinct correlations. Furthermore, Ferraris *et al.* (1999) proposed a separate correlation for the Li-bearing minerals of the milarite group (sugilite, brannockite, sogdianite, and darapiosite): <*A*–O> = 1.38(5) + 0.93(7) $<r_A>$. For Li- and Zn-bearing minerals of the milarite group (Table 7), addition of our data on the end-member sogdianite structure and sogdianite (Cooper *et al.* 1999) produces a refined correlation: <*A*–O> = 1.411 + 0.901 $<r_A>$, with R^2 = 0.974 (Fig. 2). This equation fits the correlations reported by Ferraris *et al.* (1999) and Hawthorne *et al.* (1991) within the estimated standard deviations. Both Na-free minerals, brannockite and sogdianite (Table 7), deviate from linearity by approximately the same value (Fig. 3). We believe that this deviation results from the common feature of both structures, the vacancy dominant at the *B* site. Cooper *et al.* (1999) divided the Li-bearing members of the milarite group into two subgroups: (1) those with a vacancy at the *B* site, and (2) those with (Na,K) at the *B* site. There is a third Li-bearing mineral with a vacancy at the *B* site, berezanskite $Ti^{4+}_2\,\square_2\,K\,[Li_3\,Si_{12}\,O_{30}]$ (Pautov & Agakhanov 1997); its structure is still unrefined.

COUPLED SUBSTITUTION OF CATIONS IN Li-BEARING MINERALS OF THE MILARITE GROUP

The shorter *T*(2)–O(3) distance in end-member sogdianite compared to that in sogdianite (Cooper *et al.*

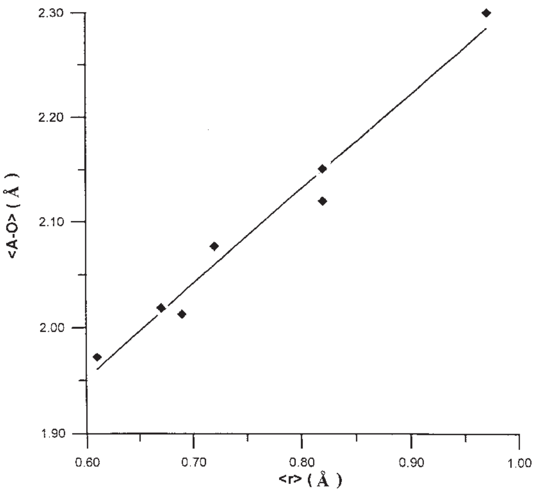

FIG. 3. Variation in <*A*–O> as a function of constituent-cation radius at the *A* site for Li- and Zn-bearing minerals having the milarite-type structure.

1999) results from the necessary bond-valence requirements at the O(3) site. The O(3) anion receives bond-valence from the *A*, *B*, *T*(1) and *T*(2) cations (Table 7). With increasing bond-valence at the *A* site, the bond valence at the *B* and *T*(2) sites should decrease. In the structure of end-member sogdianite, there is no cation at the *B* site, and thus the increase in bond-valence (0.67 *vu*, valence units, for end-member sogdianite compared with 0.60 *vu* for sogdianite) compensates for the lack of bond-valence incident from the *B* site. A small decrease in the *T*(2)–O bond slightly increases the bond-valence to O(3) and compensates for the vacancy at the *B* site. The same dependence of the *T*(2)–O bond on the *B*-site population for sugilite and brannockite has been emphasized by Hawthorne *et al.* (1991). In sugilite, the <*T*(2)–O> bond-length is 1.970 Å ($\square_{1.02}Na_{0.98}$), whereas in brannockite, the <*T*(2)–O> distance is 1.922 Å ($\square$ dominant at the *B* site) (Table 6). Of course, this effect is less pronounced in sogdianite crystals because of a smaller difference of *A*-cation bond-valence compared to sugilite ($A = Fe^{3+}_{1.66}Al^{3+}_{0.34}$) and brannockite ($A = Sn^{4+}_{2}$).

On the Isomorphous Series Sugilite–Sogdianite

In accordance with Armbruster & Oberhänsli (1988), the *a* and *c* parameters of sogdianite increase as both the common edge between the *T*(2) tetrahedron and the *A* octahedron and the *C*–O bond length become longer: a = 10.1240(3), c = 14.3198(5) Å, V = 1271.1(1) Å^3 for end-member sogdianite *versus* a = 10.053(1), c = 14.211(2) Å, V = 1243.8(4) Å^3 for sogdianite (Cooper *et al.* 1999).

A linear correlation of cell parameters *versus* chemical composition has been established recently for the sugilite–sogdianite isomorphous series (Pautov *et al.* 2000). More than 50 samples from Dara-i-Pioz have been analyzed by electron-microprobe analysis and X-ray powder diffraction, and reveal a continuous sugilite–sogdianite solid-solution series. The data confirm the existence of ideal end-member sogdianite. Table 8 presents revised end-member formulae for Li- and Zn-bearing minerals of the milarite-type structure.

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TABLE 8. END-MEMBER FORMULAE FOR Li- AND Zn-BEARING MINERALS WITH THE MILARITE-TYPE STRUCTURE

	A	*B*	*C*	*T*(2)	*T*(1)
Sogdianite	Zr_2	$\square_2$	K	Li_3	Si_{12}
Brannockite	Sn_2	$\square_2$	K	Li_3	Si_{12}
Berezanskite	Ti_2	$\square_2$	K	Li_3	Si_{12}
Darapiosite	$Mn^{2+}Zr$	Na_2	K	Li_3	Si_{12}
Sugilite	Fe^{3+}_2	Na_2	K	Li_3	Si_{12}
Dusmatovite	Mn^{2+}_2	$\square Na$	K	Zn_3	Si_{12}
Shibkovite	Ca_2	$\square K$	K	Zn_3	Si_{12}

References

Armbruster, T. & Oberhänsli, R. (1988): Crystal chemistry of double-ring silicates: structures of sugilite and brannockite. *Am. Mineral.* **73**, 595-600.

Bakakin, V.V., Balko, V.P. & Solovyeva, L.P. (1975): Crystal structure of milarite, armenite, and sogdianite. *Sov. Phys. Crystallogr.* **19**, 460-462.

Brown, I.D. & Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

Černý, P., Hawthorne, F.C. & Jarosewich, E. (1980): The crystal chemistry of milarite. *Can. Mineral.* **18**, 41-57.

Cooper, M.A., Hawthorne, F.C. & Grew, E.S. (1999): The crystal chemistry of sogdianite, a milarite-group mineral. *Am. Mineral.* **84**, 764-768.

Dusmatov, V.D., Yefimov, A.F., Katayeva, M.E., Khoroshilova, L.A. & Yanulov, K.P. (1968): Sogdianite, a new mineral. *Dokl. Acad. Sci. USSR* **182**, 137-139.

Ferraris, G., Prencipe, M., Pautov, L.A. & Sokolova, E.V. (1999): Crystal structure of darapiosite and comparison with Li- and Zn-bearing minerals of the milarite group. *Can. Mineral.* **37**, 769-774.

Forbes, W.C., Baur, W.H. & Khan, A.A. (1972): Crystal chemistry of milarite-type minerals. *Am. Mineral.* **57**, 463-472.

Hawthorne, F.C., Kimata, M., Černý, P., Ball, N., Rossman, G.R. & Grice, J.D. (1991): The crystal chemistry of the milarite-group minerals. *Am. Mineral.* **76**, 1836-1856.

Ibers, J.A. & Hamilton, W.C., eds. (1974): *International Tables for X-ray Crystallography* IV. Kynoch Press, Birmingham, U.K.

Kabalov, Yu.K., Sokolova, E.V. & Pautov, L.A. (1994): More precise determination of the crystalline structure of sogdianite by the Rietveld method. *Phys. Dokl.* **38**, 435-437.

Pautov, L.A. & Agakhanov, A.A. (1997): Berezanskite $KLi_3Ti_2Si_{12}O_{30}$, a new mineral. *Zap. Vser. Mineral. Obshchest.* **126**(4), 75-80 (in Russ.).

________, ________ & SOKOLOVA, E.V. (1998): Shibkovite, a new mineral of milarite group. *Zap. Vser. Mineral. Obshchest.* **127**(4), 89-94 (in Russ.).

________, ________, ________ & IGNATENKO, K.I. (1996): Dusmatovite, a new mineral of milarite group. *Vestnik Mosk. Univ., Ser. 4 Geol.* **N2**, 54-60 (in Russ.).

________ & KHVOROV, P.V. (1998): Bazirite from Tajikistan. *Zap. Vser. Mineral. Obshchest.* **127**(1), 80-83 (in Russ.).

________, ________, MUFTAKHOV, V.A. & AGAKHANOV, A.A. (2000): Sogdianite and sugilite from Dara-i-Pioz massif (Tajikistan). *Zap. Vser. Mineral. Obshchest.* **129**(3), 66-79 (in Russ.).

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

SHELDRICK, G.M. (1993): *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data* (3rd revision). Univ. of Göttingen, Göttingen, Germany.

________ (1996): *SADABS User Guide*, Univ. of Göttingen, Göttingen, Germany.

SOKOLOVA, E.V. & PAUTOV, L.A. (1995): Crystal structure of dusmatovite. *Phys. Dokl.*. **40**, 607- 610.

________, RYBAKOV, V.B. & PAUTOV, L.A. (1999): Crystal structure of shibkovite. *Dokl. Earth Sci.* **369A**, 1288-1291.

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