The crystal structure of baratovite[1]

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Abstract

The crystal structure of baratovite has been determined and refined from 4654 single-crystal diffractometer data by means of direct methods and least-squares refinements with anisotropic thermal parameters, giving $R = 0.034$. The structure consists of Si_6O_{18} rings connected by dense Ca-octahedral sheets and by Ti-octahedra, Li-tetrahedra, and 12-fold K-polyhedra. The chemical formula derived from the structural study is $KLi_3Ca_7(Ti,Zr)_2[Si_6O_{18}]_2F_2$. Analysis of the experimental values shows that in baratovite there is no correlation between Si–O(br) distances and Si–O(br)–Si angles. Positive correlations between Si–O distances and $\langle O-Si-O\rangle_3$ angles as well as between the Si–O bond length variation and the bond strength variation are found. Our results confirm the structural model published by Sandomirskii *et al.* (1976) as this investigation was approaching completion.

Introduction and experimental

Baratovite is a new silicate found as an accessory mineral in quartz–albite–aegirine pegmatitic veinlets in quartz–aegirine syenites and albitites of the Dara-Pioz alkalic massif, Tadzhikistan (USSR). The mineral has been described by Dusmatov *et al.* (1975), who gave optical and physical properties, IR spectrum, crystal data, and a chemical analysis leading to an idealized formula $KLi_2Ca_8Ti_2Si_{12}O_{37}F$.

A colorless cleavage fragment with the shape of an irregular cube of about 0.3mm was used for our work. A preliminary crystallographic study by Weissenberg photography confirmed both the lattice parameters and the crystal symmetry obtained by the above-mentioned authors. Final lattice parameters were determined from the scattering angles of 25 high-angle reflections, measured on a Philips single-crystal diffractometer. Crystal data are given in Table 1. Intensity data were collected on the same computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy) with $MoK\alpha$ radiation and the ω–2θ scan technique. Of 4654 reflections scanned within the range $2° < \theta < 30°$, 4011 were considered to be actually observed according to

the criterion $I > 4\sigma(I)$. Absorption was considered negligible.

The structure was solved with the MULTAN program (Germain *et al.*, 1971) which was used in its fully automatic mode. Positional and isotropic thermal parameters were refined by full-matrix least-squares cycles down to an R index of 0.040. A weight $1/\sqrt{\sigma}$, with σ deriving from counting statistics, was given to all observed reflections. Two further cycles with anisotropic thermal parameters led to a final R index of 0.034. Atomic scattering factors used in the structure-factor calculation are those given in the *International Tables for X-ray Crystallography* (1974, p. 99–101). Final atomic and equivalent isotropic thermal parameters are given in Table 2, while bond distances and angles are listed in Table 3. Observed and calculated structure factors and anisotropic temperature factors are listed in Tables 4 and 5 respectively[2].

Discussion of the structure

In baratovite six-membered Si_6O_{18} rings are present. As shown in Figure 1, which represents a projec-

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Table 1. Crystal data

Formula: $Li_3Ca_7(Ti_{0.87}Zr_{0.13})_2[Si_6O_{18}]_2F_2$

FW	1398.5
Unit cell dimensions:	a = 16.941(3) A
	b = 9.746(2)
	c = 20.907(3)
	β = 112.50(10)°
Cell volume	3189.1 A^3
Space group:	C2/c
Z:	4
Dm:	2.92 g cm^{-3} (*)
Dx:	2.912 g cm^{-3}
μ (MoKα):	30.1 cm^{-1}
Crystal size:	~0.3 x 0.3 x 0.3 mm

(*) Value given by Dusmatov et al. (1975)

tion of the structure along [102], pairs of rings are superimposed in this direction; the rotation angle between the two is about 30°. In Figure 2 an *ac* projection of the structure is given. In the [102] direction the Si–O rings are connected on one side by means of a dense Ca-octahedral sheet and on the other by means of Ti-octahedra, distorted Li-tetrahedra, and irregular 12-fold K-polyhedra.

The present results confirm the structural model presented by Sandómirskii *et al.* (1976), in a paper which appeared when this investigation was approaching completion. Our study, however, provides higher precision in interatomic distances and angles. This is due to the higher number of reflections used and to the better F_o–F_c agreement reached in the refinements.

An improvement in the *R* index was also achieved by taking into account the presence of Zr in baratovite. Bykova's chemical analysis (Dusmatov *et al.*, 1975) gives ZrO_2 = 2.28 percent; assuming that all Zr substitutes for Ti, an atomic ratio Zr/Ti = 0.15 (87 percent Ti, 13 percent Zr) results. Another indication of the presence of Zr in the Ti atomic sites is given by the temperature factor. In fact, considering this position fully occupied by Ti, *B* turned negative during the refinement. Occupancy refinement led to a Zr/Ti atomic ratio very similar to that computed from the analysis; the temperature factor for (Ti,Zr) became positive definite and the *R* index improved.

The amount of fluorine in baratovite, determined by Bykova, is not enough to justify the two atoms in

the formula given by Sandomirskii *et al.* (1976). On the other hand the assumption of OH substituting for F is not supported by experimental evidence. In fact the examination of the interatomic distances around the F position does not show values suitable for H-bonding; moreover in the difference Fourier synthesis there are no maxima attributable to H atoms. Table 3 shows that the three Ca–F bond lengths are shorter than the Ca–O bond lengths. In the Ca(1), Ca(2), and Ca(4) octahedra, the differences between Ca–F and the mean values of Ca–O are 0.083, 0.112, and 0.143A respectively. These figures are close to the difference between the effective ionic radii of O^{2-} and F^- (Shannon, 1976). A further attempt to clarify this

Table 2. Fractional atomic coordinates and isotropic thermal parameters

Atom	x	y	z	B eq.*
Ti	.33460(2)	.07052(3)	.25190(2)	0.36
Ca(1)	.22017(3)	−.07256(4)	.51329(2)	0.62
Ca(2)	.14518(3)	.28319(4)	.50695(2)	0.64
Ca(3)	.07260(3)	.63830(4)	.50006(2)	0.58
Ca(4)	.00	.00	.50	0.60
K	.00	.07116(9)	.25	2.52
Si(1)	.61404(4)	.26552(6)	.36061(3)	0.46
Si(2)	.43105(3)	.32388(6)	.36004(3)	0.46
Si(3)	.36923(3)	.63544(6)	.35952(3)	0.47
Si(4)	.49150(3)	.87983(6)	.36058(3)	0.46
Si(5)	.67409(3)	.81512(6)	.35930(3)	0.46
Si(6)	.73852(3)	.50777(6)	.36230(3)	0.46
O(1)	.65859(9)	.40248(15)	.34516(8)	1.05
O(2)	.65949(9)	.22375(15)	.44124(7)	0.78
O(3)	.61253(9)	.14422(15)	.30831(8)	0.83
O(4)	.51498(9)	.30992(16)	.34054(8)	0.94
O(5)	.35284(9)	.24005(15)	.30572(7)	0.81
O(6)	.45297(9)	.28340(16)	.43964(7)	0.91
O(7)	.41045(10)	.48836(16)	.35154(9)	1.23
O(8)	.27384(9)	.65317(15)	.30411(8)	0.89
O(9)	.37909(9)	.65109(15)	.43871(7)	0.92
O(10)	.42732(9)	.74862(15)	.34060(8)	0.95
O(11)	.52081(9)	.92000(15)	.44137(7)	0.80
O(12)	.44899(9)	1.00464(16)	.30851(8)	0.75
O(13)	.57291(10)	.82063(18)	.34558(9)	1.07
O(14)	.72900(10)	.85295(17)	.43888(8)	0.89
O(15)	.69539(9)	.90634(17)	.30421(8)	0.81
O(16)	.69225(10)	.65698(17)	.34453(8)	1.03
O(17)	.78585(9)	.47590(17)	.31054(8)	0.79
O(18)	.80087(10)	.49875(17)	.44299(8)	0.87
F	.10199(8)	.06911(14)	.45949(7)	1.14
Li(1)	.50	.0843(6)	.25	0.90
Li(2)	.2465(3)	.3181(5)	.2488(2)	1.00

*B eq.'s are the equivalent values after Hamilton (1959)

Table 3. Interatomic distances (A) and angles (°)

Ca octahedra

Ca(1)	- F	2.336		Ca(2)	- F	2.306
	O(2,3)	2.466			O(6,7)	2.419
	O(2,5)	2.398			O(11,3)	2.426
	O(9,7)	2.390			O(14,3)	2.460
	O(14,4)	2.380			O(14,4)	2.396
	O(18,3)	2.460			O(18,4)	2.391
Mean		2.405		Mean		2.400

Ca(3)	- O(2,2)	2.400		Ca(4)	- F	2.297 x 2
	O(6,2)	2.397			O(6,3)	2.432 x 2
	O(9,6)	2.392			O(9,3)	2.449 x 2
	O(11,3)	2.445		Mean		2.393
	O(11,6)	2.410				
	O(18,4)	2.417				
Mean		2.410				

Ti polyhedron

Ti	- O(3,9)	1.941
	O(5)	1.956
	O(8,8)	1.936
	O(12,1)	1.953
	O(15,10)	1.933
	O(17,3)	1.952
Mean		1.945

O(3,9) - O(5)	2.823	O(3,9) - Ti - O(5)	92.9
O(3,9) - O(8,8)	2.768	O(3,9) - Ti - O(8,8)	91.2
O(3,9) - O(12,1)	2.636	O(3,9) - Ti - O(12,1)	85.3
O(3,9) - O(15,10)	2.728	O(3,9) - Ti - O(15,10)	89.5
O(5) - O(8,8)	2.611	O(3,9) - Ti - O(17,3)	173.5
O(5) - O(12,1)	2.801	O(5) - Ti - O(8,8)	84.3
O(5) - O(17,3)	2.831	O(5) - Ti - O(12,1)	91.6
O(8,8) - O(15,10)	2.748	O(5) - Ti - O(15,10)	174.3
O(8,8) - O(17,3)	2.810	O(5) - Ti - O(17,3)	92.8
O(12,1) - O(15,10)	2.835	O(8,8) - Ti - O(12,1)	174.4
O(12,1) - O(17,3)	2.793	O(8,8) - Ti - O(15,10)	90.5
O(15,10) - O(17,3)	2.626	O(8,8) - Ti - O(17,3)	92.6
		O(12,1) - Ti - O(15,10)	93.7
		O(12,1) - Ti - O(17,3)	91.4
		O(15,10) - Ti - O(17,3)	90.5

Li tetrahedra

Li(1)	- O(3)	1.918 x 2
	O(12,1)	1.911 x 2
Mean		1.915

O(3) - O(3,9)	3.656	O(3) - Li(1) - O(3,9)	144.6
O(3) - O(12,1)	3.087 x 2	O(3) - Li(1) - O(12,1)	107.4 x 2
O(3) - O(12,10)	2.637 x 2	O(3) - Li(1) - O(12,10)	87.0 x 2
O(12,1) - O(12,10)	3.494	O(12,1)-Li(1)- O(12,10)	132.1

Li(2)	- O(5)	1.897
	O(8,8)	1.906
	O(15,3)	1.896
	O(17,9)	1.919
Mean		1.905

O(5) - O(8,8)	2.611	O(5) - Li(2) - O(8,8)	86.7
O(5) - O(15,3)	3.110	O(5) - Li(2) - O(15,3)	110.2
O(5) - O(17,9)	3.513	O(5) - Li(2) - O(17,9)	134.0
O(8,8) - O(15,3)	3.520	O(8,8) - Li(2) - O(15,3)	135.5
O(8,8) - O(17,9)	3.151	O(8,8) - Li(2) - O(17,9)	110.9
O(15,3) - O(17,9)	2.626	O(15,3) - Li(2) - O(17,9)	87.0

K polyhedron

K	- O(1,3)	3.128 x 2
	O(4,3)	3.124 x 2
	O(7,3)	3.150 x 2
	O(10,3)	3.143 x 2
	O(13,3)	3.089 x 2
	O(16,3)	3.207 x 2
Mean		3.140

Si - Si distances

Si(1) - Si(2)	3.147
Si(2) - Si(3)	3.211
Si(3) - Si(4)	3.151
Si(4) - Si(5)	3.167
Si(5) - Si(6)	3.180
Si(6) - Si(1)	3.157

Si-O-Si and Si-Si-Si angles

Si(1) - O(1) - Si(6)	152.3	Si(6) - Si(1) - Si(2)	121.2
Si(1) - O(4) - Si(2)	150.7	Si(1) - Si(2) - Si(3)	119.4
Si(2) - O(7) - Si(3)	158.8	Si(2) - Si(3) - Si(4)	120.1
Si(3) - O(10) - Si(4)	151.5	Si(3) - Si(4) - Si(5)	119.4
Si(4) - O(13) - Si(5)	152.7	Si(4) - Si(5) - Si(6)	121.1
Si(5) - O(16) - Si(6)	156.2	Si(5) - Si(6) - Si(1)	118.9

Si tetrahedra

Si(1)	- O(1)	1.625
	O(2)	1.614
	O(3)	1.604
	O(4)	1.625
Mean		1.617

O(1) - O(2)	2.654	O(1) - Si(1) - O(2)	110.0
O(1) - O(3)	2.660	O(1) - Si(1) - O(3)	110.9
O(1) - O(4)	2.561	O(1) - Si(1) - O(4)	104.0
O(2) - O(3)	2.695	O(2) - Si(1) - O(3)	113.7
O(2) - O(4)	2.680	O(2) - Si(1) - O(4)	111.7
O(3) - O(4)	2.578	O(3) - Si(1) - O(4)	106.0
Mean	2.638		

Si(2)	- O(4)	1.628
	O(5)	1.600
	O(6)	1.609
	O(7)	1.636
Mean		1.618

O(4) - O(5)	2.647	O(4) - Si(2) - O(5)	110.2
O(4) - O(6)	2.670	O(4) - Si(2) - O(6)	111.1
O(4) - O(7)	2.554	O(4) - Si(2) - O(7)	103.0
O(5) - O(6)	2.694	O(5) - Si(2) - O(6)	114.2
O(5) - O(7)	2.648	O(5) - Si(2) - O(7)	109.8
O(6) - O(7)	2.624	O(6) - Si(2) - O(7)	107.9
Mean	2.640		

Si(3)	- O(7)	1.631
	O(8)	1.597
	O(9)	1.606
	O(10)	1.625
Mean		1.615

O(7) - O(8)	2.676	O(7) - Si(3) - O(8)	112.0
O(7) - O(9)	2.619	O(7) - Si(3) - O(9)	108.0
O(7) - O(10)	2.572	O(7) - Si(3) - O(10)	104.4
O(8) - O(9)	2.693	O(8) - Si(3) - O(9)	114.5
O(8) - O(10)	2.586	O(8) - Si(3) - O(10)	106.8
O(9) - O(10)	2.657	O(9) - Si(3) - O(10)	110.7
Mean	2.634		

Si(4)	- O(10)	1.626
	O(11)	1.616
	O(12)	1.607
	O(13)	1.632
Mean		1.620

O(10) - O(11)	2.679	O(10) - Si(4) - O(11)	111.5
O(10) - O(12)	2.645	O(10) - Si(4) - O(12)	109.8
O(10) - O(13)	2.527	O(10) - Si(4) - O(13)	101.8
O(11) - O(12)	2.699	O(11) - Si(4) - O(12)	113.8
O(11) - O(13)	2.660	O(11) - Si(4) - O(13)	110.0
O(12) - O(13)	2.641	O(12) - Si(4) - O(13)	109.3
Mean	2.642		

Si(5)	- O(13)	1.627
	O(14)	1.608
	O(15)	1.602
	O(16)	1.624
Mean		1.615

O(13) - O(14)	2.635	O(13) - Si(5) - O(14)	109.2
O(13) - O(15)	2.668	O(13) - Si(5) - O(15)	111.5
O(13) - O(16)	2.581	O(13) - Si(5) - O(16)	105.1
O(14) - O(15)	2.700	O(14) - Si(5) - O(15)	114.6
O(14) - O(16)	2.643	O(14) - Si(5) - O(16)	109.7
O(15) - O(16)	2.579	O(15) - Si(5) - O(16)	106.2
Mean	2.634		

Si(6)	- O(1)	1.626
	O(16)	1.626
	O(17)	1.604
	O(18)	1.614
Mean		1.618

O(1) - O(16)	2.546	O(1) - Si(6) - O(16)	103.1
O(1) - O(17)	2.622	O(1) - Si(6) - O(17)	108.6
O(1) - O(18)	2.664	O(1) - Si(6) - O(18)	110.6
O(16) - O(17)	2.644	O(16) - Si(6) - O(17)	109.9
O(16) - O(18)	2.664	O(16) - Si(6) - O(18)	110.7
O(17) - O(18)	2.690	O(17) - Si(6) - O(18)	113.5
Mean	2.638		

Symmetry code

None	x	y	z
1	x	1 + y	z
2	1/2 - x	1/2 + y	z
3	1/2 - x	1/2 - y	z
4	1 - x	1 - y	1 - z
5	1 - x	- y	1 - z
6	1/2 - x	3/2 - y	1 - z
7	1/2 - x	1/2 - y	1 - z
8	1/2 - x	-1/2 + y	1/2 - z
9	1 - x	y	1/2 - z
10	1 - x	-1 + y	1/2 - z

The standard deviations are: 0.002 Å for Si-O, Ti-O, Ca-O, K-O and O-O; 0.004 Å for Li-O; 0.001 Å for Si-Si; 0.1° for O-Si-O and O-Ti-O; 0.2° for O-Li-O; 0.1° for Si-O-Si and Si-Si-Si.
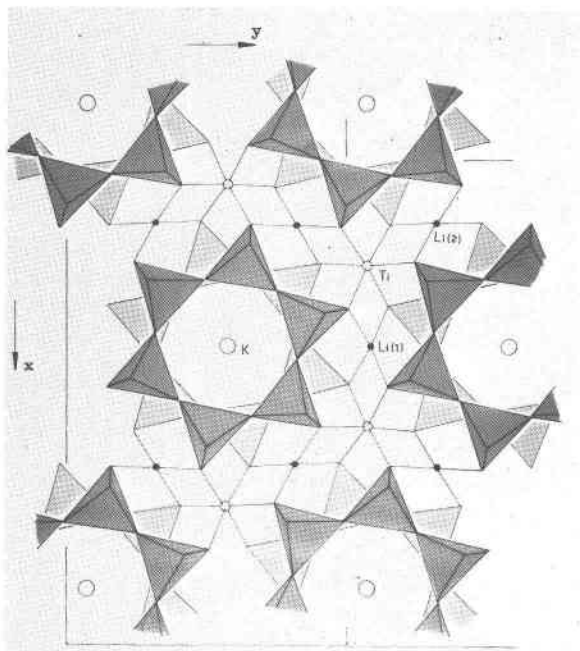
Fig. 1. A partial view of the structure, projected along [102], showing Si–O rings, Ti–O and Li–O polyhedra, and K atoms.

problem was made during the least-squares refinement. Starting from the assumption that the F position was occupied half by oxygen and half by fluorine atoms, the occupancies were allowed to vary, but the results of the refinement were unreliable, because of the similar scattering powers of O and F. In fact two successive cycles gave occupancy values shifting in opposite directions.
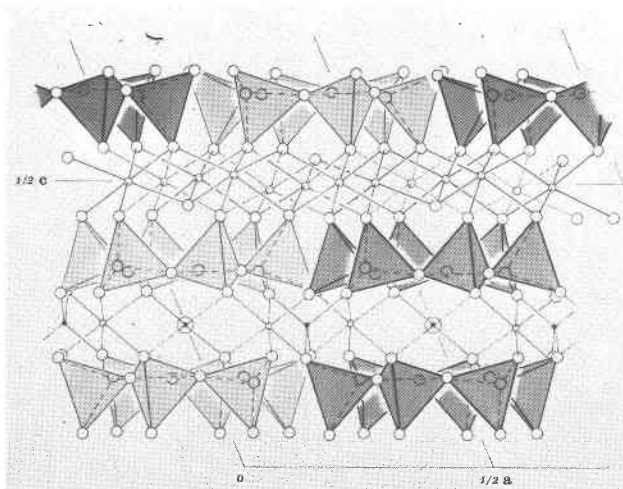

Fig. 2. An *ac* projection of the structure. At $1/2\ c$ a portion of a Ca-octahedral sheet is outlined. Between the Si–O rings, at $1/4\ c$, the Li tetrahedra (solid circles), Ti octahedra (open circles), and K atoms (large open circles) are represented.

In Table 6 an electrostatic valence balance, computed according to the method of Brown and Shannon (1973), is given. Since this method applies to oxides, all distances involving the F atom, namely Ca(1)–F, Ca(2)–F and Ca(4)–F, were artificially increased by 0.08A in order to take into account the difference between the O^{2-} and F^- effective ionic radii. The balance is quite satisfactory not only for oxygens (maximum deviation 3.0 percent) but also for fluorine, thus confirming that the F sites are truly occupied by fluorine atoms. In the balance computation three long Ca–O distances, namely Ca(2)–O(13,6) = 3.139A, Ca(4)–O(7,6) and Ca(4)–O(7,14) = 2.889A were omitted. The general charge balance is not substantially modified by taking into account these long Ca–O distances; only minor changes take place and often not in the right direction. Consequently, the chemical formula derived from the present structural study is KLi_3Ca_7 $(Ti_{0.87}Zr_{0.13})_2[Si_6O_{18}]_2F_2$.

Consideration of the Si–O bond lengths and angles

As one can see from Table 3, the Si–O(br) bridging bond lengths, which range from 1.624 to 1.636A, are all greater than the Si–O(nbr) bond lengths, which range from 1.597 to 1.616A. The two mean values are 1.628 and 1.607A respectively, while the overall Si–O mean bond distance is 1.618A. The Si$\cdots$Si distances within the ring vary from 3.147 to 3.211A, with a mean value of 3.169A. Recently O'Keeffe and Hyde (1978), in a paper dealing with Si–O–Si configurations in silicates, published a histogram showing the distribution of 141 nearest-neighbors Si$\cdots$Si in various silicates and silicas. The minimum and maximum values are 2.94 and 3.27A, with a pronounced peak at 3.06A and a clearly skewed distribution. The values found in baratovite fall on the right tail of the histogram.

The six independent Si tetrahedra show O–Si–O angles ranging from 101.8° to 114.6°; the smallest angle in each tetrahedron is the one involving two bridging oxygen atoms which are shared with the K polyhedron. The bridging Si–O–Si angles show values ranging from 150.7° to 158.8° with a mean value of 151.3°.

Many authors (*e.g.* Brown *et al.*, 1969; O'Keeffe and Hyde, 1978; Baur, 1971, 1977) have studied the relationships between Si–O(br) bond distances and Si–O(br)–Si angles. Because of the low number of independent observations and the fact that individual Si–O(br) and Si–O(br)–Si values are clustered around the mean value, it is not very meaningful to check

Table 6. Electrostatic valence balance

Atom	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	Li(1)	Li(2)	Ti	Ca(1)	Ca(2)	Ca(3)	Ca(4)	K	Sums
O(1)	0.98					0.98								0.08	2.04
O(2)	1.01									0.30 0.35		0.34			2.00
O(3)	1.03				0.25				0.67						1.95
O(4)	0.98	0.97												0.09	2.04
O(5)		1.05					0.26	0.65							1.96
O(6)		1.03									0.33	0.34	0.32		2.02
O(7)		0.95	0.96											0.08	1.99
O(8)			1.05				0.25	0.68							1.98
O(9)			1.02							0.36		0.35	0.31		2.04
O(10)			0.97	0.98										0.08	2.03
O(11)				1.01							0.32	0.33 0.31			1.97
O(12)				1.04	0.25			0.66							1.95
O(13)				0.97	0.97									0.09	2.03
O(14)					1.02					0.36		0.30 0.35			2.03
O(15)					1.04		0.25	0.68							1.97
O(16)					0.97	0.97								0.08	2.02
O(17)						1.04	0.24	0.66							1.94
O(18)						1.01				0.30	0.35	0.33			1.99
F										0.33	0.35		0.37		1.05

baratovite for a correlation between Si–O(br) and Si–O(br)–Si. However, an attempt shows that in baratovite this correlation is very poor and not in the expected direction. In fact the same Si–O(br) bond length is found for the bridging atoms O(1), O(10) and O(16), while the corresponding Si–O(br)–Si angles are 152.3°, 151.5° and 156.2°. Moreover, against all expectation, the largest Si–O(br)–Si angle (158.8°) corresponds to the longest Si–O(br) distances (1.636 and 1.631A). This result seems to be in agreement with that outlined by O'Keeffe and Hyde (1978) who found no correlation between d(Si–O) and the Si–O–Si angle when the angle involved is greater than 145°.

A second kind of diagram, often found in papers dealing with silicate structures, is that relating d(Si–O) with $\langle O–Si–O \rangle_3$ (the mean of the three O–Si–O angles common to the bond). As shown in Figure 3, an interesting feature of this diagram for baratovite is the splitting of the experimental points into two well-separated populations: one related to the bridging oxygen atoms, the other related to the non-bridging ones. The regression line referring to all 24 experimental points shows a good correlation ($r = 0.85$) comparable with the one found, for example, in rosenhahnite (Wan *et al.*, 1977). This regression line, however, is no longer consistent with the distribution
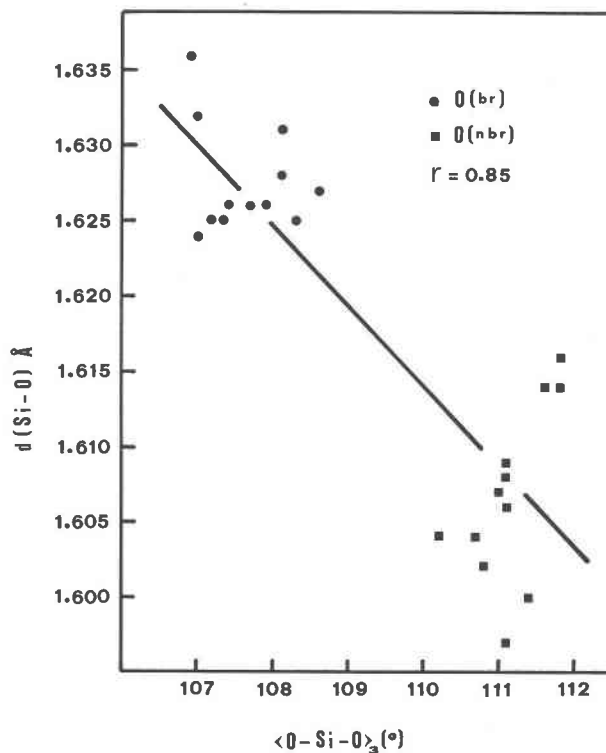

Fig. 3. Observed Si–O bond lengths d(Si–O), plotted against the average values of the three O–Si–O angles common to each bond.

Table 7. Δp_o, Si–O distances, Δd(oc) and Δd(om) calculated after Baur (1971)

	Δp_o	d_{calc}	Δd(oc)	Δd(om)
Si(1)–O(1)	0.0625	1.623	0.002	0.008
O(2)	−0.0225	1.615	−0.001	−0.003
O(3)	−0.1025	1.608	−0.004	−0.013
O(4)	0.0625	1.623	0.002	0.008
Si(2)–O(4)	0.0625	1.624	0.004	0.010
O(5)	−0.1025	1.609	−0.009	−0.018
O(6)	−0.0225	1.615	−0.006	−0.009
O(7)	0.0625	1.624	0.012	0.018
Si(3)–O(7)	0.0625	1.621	0.010	0.016
O(8)	−0.1025	1.606	−0.009	−0.018
O(9)	−0.0225	1.613	−0.007	−0.009
O(10)	0.0625	1.621	0.004	0.015
Si(4)–O(10)	0.0625	1.626	0.000	0.006
O(11)	−0.0225	1.618	−0.002	−0.004
O(12)	−0.1025	1.611	−0.004	−0.013
O(13)	0.0625	1.626	0.006	0.012
Si(5)–O(13)	0.0625	1.621	0.006	0.012
O(14)	−0.0225	1.613	−0.005	−0.007
O(15)	−0.1025	1.606	−0.004	−0.013
O(16)	0.0625	1.621	0.003	0.009
Si(6)–O(1)	0.0625	1.623	0.003	0.008
O(16)	0.0625	1.623	0.003	0.008
O(17)	−0.1025	1.608	−0.004	−0.014
O(18)	−0.0225	1.615	−0.001	−0.004

Fig. 4. Bond length variation Δd(om) vs. Δp_o for the 24 values of Si–O bond lengths in baratovite. Superimposed points are split along the abscissa.

and 0.010A respectively. This is probably related to the coordination of Ca(4), which binds six anions in an irregular octahedron (mean distance 2.393A) and two more O(7) atoms at a distance of 2.889A. Owing to the long interatomic distance the contribution of Ca(4) was not taken into account in the computation of the p_o value to be attributed to O(7). The agreement between the observed and calculated distances is reflected in the good correlation ($r = 0.96$) found between Δp_o and Δd(om). As shown in Figure 4 there are three separate groups of experimental points: this clearly depends upon the three kinds of coordination of the oxygen atoms.

of the experimental points when the populations are treated separately. Therefore the correlation of d(Si–O) with $\langle$O–Si–O$\rangle_3$ found in baratovite is less meaningful than appears from the r coefficient value.

In Table 7 the Si–O distances calculated as suggested by Baur (1971) are reported together with the values of Δd(oc) and Δd(om) as defined by Baur: the former as the difference between the observed and calculated distances and the latter as the difference between d(obs) for one individual anion in a coordination polyhedron around a cation and the mean d(obs) for all anions in this coordination. As can be seen from the values of Δd(oc) the observed and calculated distances are in good agreement; the mean value of Δd(oc) is 0.005A. The highest discrepancies are found in the distances related to O(7), i.e. Si(2)–O(7) and Si(3)–O(7), where the Δd(oc)'s are 0.012
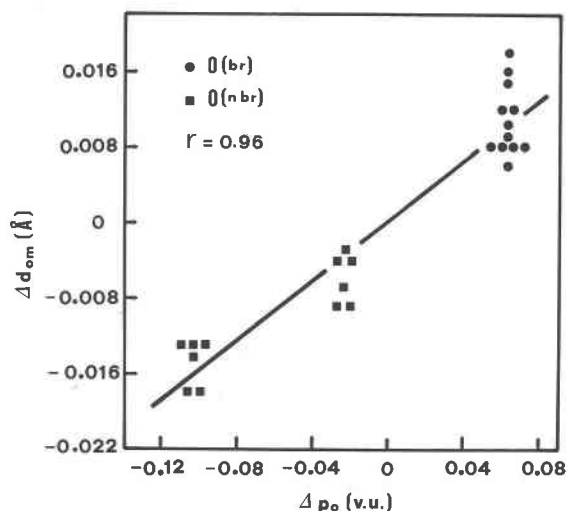
References

Baur, W. H. (1971) The prediction of bond length variations in silicon–oxygen bonds. Am. Mineral., 56, 1573–1599.
———— (1977) Silicon–oxygen bond lengths, bridging angles Si–O–Si and synthetic low tridymite. Acta Crystallogr., B33, 2615–2619.
Brown, G. E., G. V. Gibbs and P. H. Ribbe (1969) The nature and the variation in length of the Si–O and Al–O bonds in framework silicates. Am. Mineral., 54, 1044–1061.
Brown, I. D. and R. D. Shannon (1973) Empirical bond-strength bond-length curves for oxides. Acta Crystallogr., A29, 266–282.
Dusmatov, V. D., E. I. Semenov, A. P. Khomayakov, A. V. Bykova and N. Zh. Dzharfarov (1975) Baratovite, a new min-

eral. *Zap. Vses. Mineral. Obshch., 104,* 580–582. (not seen; extracted from *Am. Mineral., 61,* 1053, 1976).

Germain, G., P. Main and M. M. Woolfson (1971) The application of phase relationships to complex structures III. The optimum use of phase relationships. *Acta Crystallogr., A27,* 368–376.

Hamilton, W. C. (1959) On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr., 12,* 609–610.

International Tables for X-Ray Crystallography (1974), vol. IV. Kynoch Press, Birmingham.

O'Keeffe, M. and B. G. Hyde (1978) On Si–O–Si configurations in silicates. *Acta Crystallogr., B34,* 27–32.

Sandomirskii, P. A., M. A. Simonov and N. V. Belov (1976) The crystal structure of baratovite, $KLi_3Ca_7Ti_2[Si_6O_{18}]_2F_2$. (in Russian) *Dokl. Akad. Nauk SSSR, 231,* 615–618.

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

Wan, C., S. Ghose and G. V. Gibbs (1977) Rosenhahnite, $Ca_3Si_3O_8(OH)_2$: Crystal structure and the stereochemical configuration of the hydroxylated trisilicate group, $[Si_3O_8(OH)_2]$. *Am. Mineral., 62,* 503–512.