MINERALOGICAL JOURNAL, VOL. 8, NO. 5, PP. 286–298, JAN. 1977

The refinement of the crystal structure of cuspidine

S. SABURI, A. KAWAHARA and C. HENMI

Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima, Okayama 700

I. KUSACHI

Department of Earth Sciences, School of Education, Okayama University, Tsushima, Okayama 700

K. KIHARA

Department of Earth Sciences, Faculty of Science, Kanazawa University, Maruno-uchi, Kanazawa 920

ABSTRACT

The crystal structure of natural cuspidine ($Ca_4(F, OH)_2Si_2O_7$) has been refined by full-matrix least-squares method to an R value of 0.042 using 1923 reflections. The crystal is monoclinic, $P2_1/a$, with $a=10.906(5)$ Å $b=10.521(6)$ Å, $c=7.518(3)$ Å, $\beta=109.30(3)°$, $Z=4$. The structure originally determined by Smirnova *et al.* (1955) is basically correct. Cuspidine is a sorosilicate, in which Si_2O_7 groups are elongated parallel to the a-axis. The distances of bridging bonds Si–O are significantly longer than those of non-bridging bonds. The calcium atoms which connect these Si_2O_7 groups have six, seven and eight nearest neighbours of oxygen atoms, although Smirnova *et al.* considered that all calcium atoms were six coordinated. These calcium polyhedra form the columns and these columns are linked to form three-dimensional networks.

Introduction

The crystal structure of cuspidine ($Ca_4(F, OH)_2Si_2O_7$) was determined by Smirnova, Rumanova and Belov (1955) and the schema of the structure is presented. According to their work, the arrange-

ment of Ca polyhedra is similar to those in the structures of ilvaite, epidote, zoisite and tilleyite, built up from edge-sharing octahedral CaO_6 chains parallel to the *a*-axis. Above all, the similarity in the structure between tilleyite and cuspidine are remarkable. The refinement of the structure of tilleyite was carried out by Louisnathan and Smith (1970). However, no further detailed structural study of cuspidine has been carried out since 1955.

In view of this, it was considered to be necessary to refine the crystal structure of cuspidine to determine the coordination states of calcium atoms and the configuration of Si_2O_7 groups more precisely.

The present authors are also interested in comparing the Si–O distances of cuspidine with other calcium silicates which contain atoms of other coordination states.

Experimental

The specimen used in this investigation was from the spurrite-gehlenite skarn in Fuka, Okayama Pref. (Henmi *et al.*, 1975). The chemical formula is determined as $Ca_4(F_{1.5}, OH_{0.5})Si_2O_7$, according to the method developed by Numano *et al.* (1976). A crystal having approximately the shape of a sphere ($r=0.1$ mm) was cautiously obtained under the polarizing microscope.

The oscillation as well as the Weissenberg photographs were taken about the *a*-, *b*- and *c*-axes, and approximate lattice parameters and extinction rules were estimated.

The intensities of the reflections were measured on an automated Philips PW-1100 four-circle diffractometer using 2θ–ω scan technique and MoKα radiation ($\lambda=0.70926$ Å) with a graphite monochromator. Of a total of 2203 intensities measured up to $2\theta=56°$, 1923 were classified as observed with $I>3\sigma$ above background. The intensity data were converted to structure factors by applying

the Lorentz-polarization correction. Also, spherical absorption corrections were made in the usual way. The crystal data measured by the same diffractometer, together with those of previous work (Smirnova *et al.*, 1955) are shown in Table 1. The calculated density ρ_x for this chemical formula is 2.978, while ρ_m is 2.96.

Table 1. The crystallographic data of cuspidine.

	This work	Smirnova *et al.* (1955) Original data	Standard setting*
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a	10.906(5) Å	7.51 KX	10.83 Å
b	10.521(6) Å	10.39 KX	10.41 Å
c	7.518(3) Å	10.81 KX	7.53 Å
β	109.30(3)°	69.93°	110.07°

* The cell parameters were transformed by the following matrix (001/010/$\bar{1}$00)

The atomic coordinates of Smirnova *et al.* (1955) were used as starting parameters for the refinement. The cell parameters were also transformed into those of Smirnova *et al.* by the matrix (00$\bar{1}$/010/100). After several cycles of full-matrix least-squares refinement, the R was reduced to 0.065 using isotropic temperature factors. And then, the refinement using anisotropic temperature factors reduced the R to 0.042. The final positional and thermal parameters are listed in Table 2 and 3, respectively. Table 4 shows the interatomic distances and bond angles of cuspidine obtained by this investigation.

Throughout the work, the calculations were carried out on the computer NEAC 2200/500 at Okayama University and also HITAC 8800/8700 at the University of Tokyo (Sakurai, T., ed., 1971).

Table 2. Final atomic coordinates and anisotropic temperature factors in cuspidine; standard deviations in parentheses. The multiplicities are all four.

Atom	X	Y	Z	$B11$	$B22$	$B33$	$B12$	$B31$	$B23$
Ca(1)	.16829(8)	.13451(5)	.42579(6)	.01033(12)	.00475(6)	.00553(6)	−.00030(6)	−.00294(6)	.00039(4)
Ca(2)	.66185(8)	.13010(6)	.41391(6)	.00949(12)	.00477(6)	.00589(6)	.00003(6)	−.00256(6)	.00043(4)
Ca(3)	.46733(8)	.41443(5)	.32002(6)	.01003(12)	.00440(5)	.00676(6)	−.00026(6)	−.00369(6)	.00041(4)
Ca(4)	.96777(8)	.40429(5)	.30375(6)	.00986(12)	.00453(5)	.00548(5)	−.00012(6)	−.00280(6)	.00035(4)
Si (1)	.27263(11)	.19354(7)	.13238(7)	.00892(14)	.00426(6)	.00498(7)	−.00007(7)	−.00249(8)	.00007(5)
Si (2)	.84667(11)	.19123(7)	.12271(7)	.00888(14)	.00439(6)	.00483(7)	−.00006(7)	−.00245(8)	.00007(5)
O (1)	.06242(28)	.22547(20)	.12172(21)	.01068(43)	.00534(18)	.00804(22)	−.00049(22)	−.00417(25)	.00069(16)
O (2)	.28644(33)	.04608(21)	.16487(25)	.01253(45)	.00470(18)	.01094(27)	−.00033(23)	−.00554(29)	.00093(17)
O (3)	.80102(32)	.04458(21)	.16033(23)	.01227(44)	.00497(19)	.00903(23)	−.00086(23)	−.00475(26)	.00108(16)
O (4)	.26934(30)	.27839(20)	.25602(19)	.01213(41)	.00537(18)	.00537(18)	−.00057(22)	−.00304(22)	−.00024(14)
O (5)	.72076(31)	.27914(21)	.24001(20)	.01191(42)	.00589(19)	.00550(18)	.00084(23)	−.00262(23)	−.00039(15)
O (6)	.40842(30)	.23932(20)	.99294(20)	.01173(41)	.00597(19)	.00522(17)	−.00076(22)	−.00236(22)	−.00009(15)
O (7)	.85795(30)	.23458(20)	.97883(20)	.01311(43)	.00552(18)	.00545(18)	.00047(22)	−.00374(23)	−.00002(15)
F (1)	.57710(27)	.49645(18)	.10434(17)	.01264(39)	.00584(16)	.00579(16)	−.00029(19)	−.00285(21)	−.00002(12)
F (2)	.07023(25)	.50358(17)	.10352(17)	.01157(37)	.00474(15)	.00551(15)	−.00009(18)	−.00301(19)	.00020(11)

Table 3. The root-mean-square amplitudes of atoms along the principal axes of the vibration ellipsoids and direction cosines of these axes with respect to the crystallographic axes.

Atom	B_{isotr}	Axes	B	r. m. s. a.	cos $\alpha 1$	cos $\alpha 2$	cos $\alpha 3$
Ca(1)	2.145	1	1.965	0.158	−0.963	0.075	−0.259
		2	2.019	0.160	−0.181	−0.891	0.416
		3	2.450	0.176	0.199	−0.447	−0.872
Ca(2)	2.168	1	1.872	0.154	−0.963	0.266	0.047
		2	2.046	0.161	−0.224	−0.885	0.409
		3	2.586	0.181	−0.151	−0.383	−0.911
Ca(3)	2.210	1	1.799	0.151	0.990	−0.030	0.135
		2	1.916	0.156	0.053	0.983	−0.175
		3	2.914	0.192	−0.128	0.181	0.975
Ca(4)	2.077	1	1.883	0.154	−0.864	0.433	−0.257
		2	1.963	0.158	−0.495	−0.824	0.276
		3	2.386	0.174	0.092	−0.365	−0.926
Si (1)	1.912	1	1.733	0.148	−0.995	−0.059	−0.076
		2	1.884	0.154	0.048	−0.989	0.142
		3	2.118	0.164	0.083	−0.138	−0.987
Si (2)	1.906	1	1.721	0.148	−0.992	−0.020	−0.127
		2	1.934	0.156	−0.016	−0.963	0.270
		3	2.062	0.162	0.128	−0.269	−0.955
O (1)	2.567	1	1.920	0.156	0.996	0.077	0.049
		2	2.285	0.170	−0.062	0.963	−0.261
		3	3.495	0.210	−0.067	0.257	0.964
O (2)	2.973	1	2.005	0.159	0.249	−0.956	0.155
		2	2.211	0.167	−0.968	−0.251	0.005
		3	4.702	0.244	0.034	−0.152	−0.988
O (3)	2.747	1	2.044	0.161	0.419	0.885	−0.202
		2	2.232	0.168	0.904	−0.385	0.187
		3	3.965	0.224	−0.088	0.261	0.961
O (4)	2.338	1	2.030	0.160	0.603	0.545	0.582
		2	2.395	0.174	−0.340	−0.485	0.806
		3	2.588	0.181	−0.722	0.684	0.107
O (5)	2.450	1	2.191	0.167	−0.516	0.531	0.672
		2	2.377	0.174	0.724	−0.148	0.674
		3	2.782	0.188	0.475	0.834	−0.308
O (6)	2.423	1	2.203	0.167	0.332	0.110	−0.937
		2	2.253	0.169	−0.772	−0.539	−0.337
		3	2.813	0.189	0.542	−0.835	0.094
O (7)	2.396	1	2.002	0.159	−0.651	0.200	−0.732
		2	2.416	0.175	0.140	−0.916	−0.375
		3	2.771	0.187	−0.746	−0.347	0.568
F (1)	2.526	1	2.435	0.176	−0.505	−0.365	−0.782
		2	2.484	0.177	−0.597	−0.506	0.622
		3	2.659	0.183	0.623	−0.782	−0.037
F (2)	2.228	1	2.063	0.162	−0.247	0.891	−0.382
		2	2.191	0.167	0.816	0.404	0.413
		3	2.429	0.175	−0.522	0.210	0.826

Table 4. Interatomic distances and bond angles of cuspidine; standard deviations in parentheses.

Si (1)-O(1)*	1.658(2)Å	-F (2)	2.311(2)
-O(2)	1.603(2)	mean	2.450
-O(4)	1.610(2)		
-O(6)	1.600(2)	O(1)-Si (1)-O(2)	110.2(1)°
mean	1.618	-O(4)	101.2(1)
		-O(6)	101.3(1)
Si (2)-O(1)*	1.659(2)Å	O(2)-Si (1)-O(4)	109.7(1)
-O(3)	1.605(2)	-O(6)	115.7(1)
-O(5)	1.609(2)	O(4)-Si (1)-O(6)	117.2(1)
-O(7)	1.609(2)	mean	109.2
mean	1.620		
		O(1)-Si (2)-O(3)	109.7(1)°
Ca(1)-O(1)	2.499(2)Å	-O(5)	101.4(1)
-O(2)	2.842(3)	-O(7)	101.3(1)
-O(4)	2.317(2)	O(3)-Si (2)-O(5)	109.3(1)
-O(6)	2.537(3)	-O(7)	117.4(1)
-O(7)	2.606(2)	O(5)-Si (2)-O(7)	116.1(1)
-F (1)	2.339(2)	mean	109.2
-F (2)	2.338(2)		
-F (2′)	2.366(2)	Si (1)-tetrahedron	
mean	2.481	O(1)-O(2)	2.674(3)Å
		O(1)-O(4)	2.526(4)
Ca(2)-O(3)	2.764(2)Å	O(1)-O(6)	2.520(3)
-O(5)	2.387(2)	O(2)-O(4)	2.627(3)
-O(6)	2.276(2)	O(2)-O(6)	2.713(3)
-O(7)	2.323(2)	O(4)-O(6)	2.740(3)
-F (1)	2.370(2)		
-F (1′)	2.342(2)	Si (2)-tetrahedron	
-F (2)	2.370(2)	O(1)-O(3)	2.669(3)Å
mean	2.405	O(1)-O(5)	2.529(3)
		O(1)-O(7)	2.526(4)
Ca(3)-O(2)	2.362(3)Å	O(3)-O(5)	2.621(3)
-O(3)	2.390(2)	O(3)-O(7)	2.746(3)
-O(4)	2.333(2)	O(5)-O(7)	2.730(3)
-O(5)	2.308(2)		
-O(6)	2.412(2)	O(1)-Ca(1)-O(2)	162.7(1)°
-F (1)	2.382(2)	-O(4)	103.0(1)
mean	2.364	-O(6)	60.1(1)
		-O(7)	59.3(1)
Ca(4)-O(1)	2.656(2)Å	-F (1)	120.1(1)
-O(2)	2.360(2)	-F (2)	74.6(1)
-O(3)	2.410(3)	-F (2′)	114.7(1)
-O(4)	2.528(2)	O(2)-Ca(1)-O(4)	60.2(1)
-O(5)	2.554(3)	-O(6)	116.3(1)
-O(7)	2.328(2)	-O(7)	110.9(1)

Table 4. (continued)

-F (1)	71.6(1)	F(1')-Ca(2)-F (2)	108.1(1)
-F (2)	112.3(1)		
-F (2')	71.0(1)	O(2)-Ca(3)-O(3)	108.4(1)°
O(4)-Ca(1)-O(6)	79.1(1)	-O(4)	166.8(1)
-O(7)	82.2(1)	-O(5)	79.6(1)
-F (1)	104.9(1)	-O(6)	106.6(1)
-F (2)	177.2(1)	-F (1)	80.3(1)
-F (2')	109.7(1)	O(3)-Ca(3)-O(4)	77.0(1)
O(6)-Ca(1)-O(7)	109.3(1)	-O(5)	162.8(1)
-F (1)	74.8(1)	-O(6)	112.5(1)
-F (2)	98.4(1)	-F (1)	83.6(1)
-F (2')	171.0(1)	O(4)-Ca(3)-O(5)	92.1(1)
O(7)-Ca(1)-F (1)	172.5(1)	-O(6)	81.4(1)
-F (2)	97.5(1)	-F (1)	88.6(1)
-F (2')	71.0(1)	O(5)-Ca(3)-O(6)	78.3(1)
F (1)-Ca(1)-F (2)	75.5(1)	-F (1)	82.9(1)
-F (2')	103.9(1)	O(6)-Ca(3)-F (1)	158.3(1)
F (2)-Ca(1)-F (2')	72.8(1)		
		O(1)-Ca(4) -O(2)	124.1(1)°
O(3)-Ca(2)-O(5)	60.7(1)°	-O(3)	121.7(1)
-O(6)	124.7(1)	-O(4)	58.3(1)
-O(7)	115.8(1)	-O(5)	58.0(1)
-F (1)	126.6(1)	-O(7)	95.9(1)
-F (1')	76.5(1)	-F (2)	72.0(1)
-F (2)	72.9(1)	O(2)-Ca(4)-O(3)	100.5(1)
O(5)-Ca(2)-O(6)	79.4(1)	-O(4)	172.0(1)
-O(7)	82.5(1)	-O(5)	74.8(1)
-F (1)	172.3(1)	-O(7)	103.1(1)
-F (1')	105.9(1)	-F (2)	81.5(1)
-F (2)	112.1(1)	O(3)-Ca(4)-O(4)	73.0(1)
O(6)-Ca(2)-O(7)	92.9(1)	-O(5)	171.5(1)
-F (1)	93.4(1)	-O(7)	109.3(1)
-F (1')	80.0(1)	-F (2)	81.0(1)
-F (2)	162.4(1)	O(4)-Ca(4)-O(5)	110.9(1)
O(7)-Ca(2)-F (1)	95.3(1)	-O(7)	83.7(1)
-F (1')	167.6(1)	-F (2)	92.6(1)
-F (2)	76.1(1)	O(5)-Ca(4)-O(7)	78.8(1)
F (1)-Ca(2)-F (1')	75.2(1)	-F (2)	91.3(1)
-F (2)	74.3(1)	O (7)-Ca (4)-F (2)	167.3(1)

* is bridging bond.

Description of the structure and discussion

According to this study, the basic structure determined by Smirnova *et al.* (1955) is correct. Figs. 1 and 2 show the projections of cuspidine parallel to the *a*- and *b*-axes, respectively. Cuspidine is a sorosilicate and the Si_2O_7 groups are elongated along the *a*-axis, as are clearly illustrated in these figures. As shown in Fig. 1, nearly all the atoms are overlapped parallel to the *a*-axis. This fact corresponds to the presence of pseudoperiod of $a'=a/2$ in the Patterson map as was pointed out by Smirnova *et al.* (1955).

Fig. 3 shows the relation between Ca polyhedra linked by edge-sharing each other connecting to Si_2O_7 group 1, 2 by edge-sharing. The Si_2O_7 groups 1, 2 are also linked to Ca polyhedra 3, 4 by corner-sharing. Fig. 4 shows the stereographic projection of the seven coordinated Ca polyhedra. Circles represent the oxygen atoms

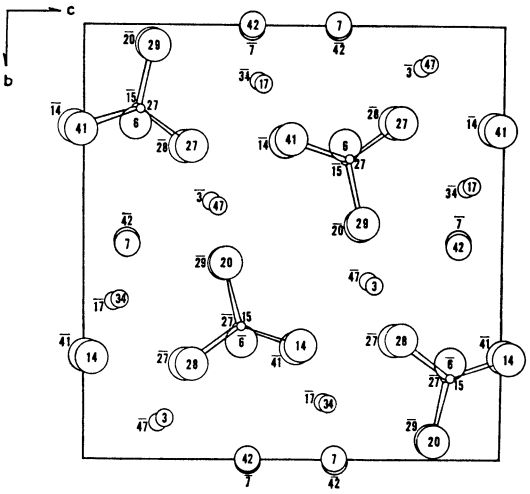

Fig. 1. Projection of the structure of cuspidine parallel to the *a*-axis. Atoms are drawn as circles from largest to smallest in the following order: oxygen, fluorine and hydroxyl, calcium and silicon. Nearly all the atoms are overlapped parallel to the *a*-axis.

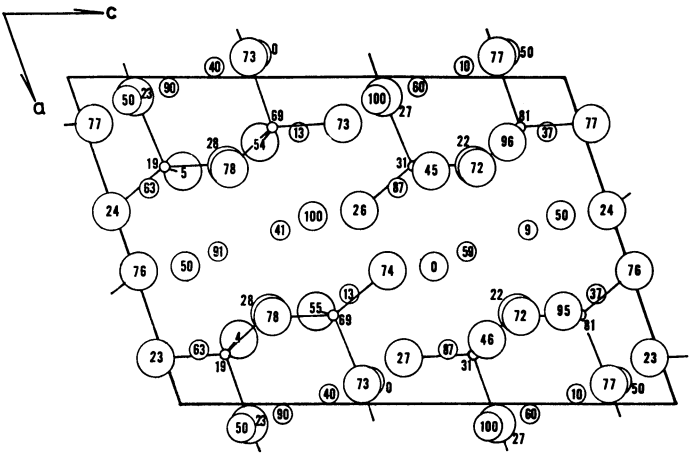

Fig. 2. Projection of the structure of cuspidine parallel to the *b*-axis. Atoms are drawn in the same way as Fig. 1. Si_2O_7 groups are elongated nearly parallel to the *a*-axis.

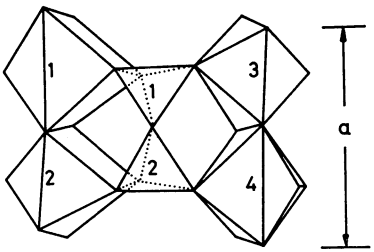

Fig. 3. The relation between Ca polyhedra and Si_2O_7 groups. The two Ca polyhedra 1, 2 are linked by edge sharing to Si_2O_7 groups 1, 2. The Si_2O_7 groups 1, 2 are alse linked to Ca polyhedra 3, 4.

around Ca (2) and triangles correspond to those of Ca (4). There is similarity in directions of the bond angles of oxygen atoms around seven coordinated calcium atoms. This fact is also observed in the case of rankinite (Saburi *et al.*, 1976). The total values of the bond angles in the Ca polyhedra are equal to 2154.6° in Ca (2), and 2121.3° in Ca (4), respectively. These two values are close to 2160°,

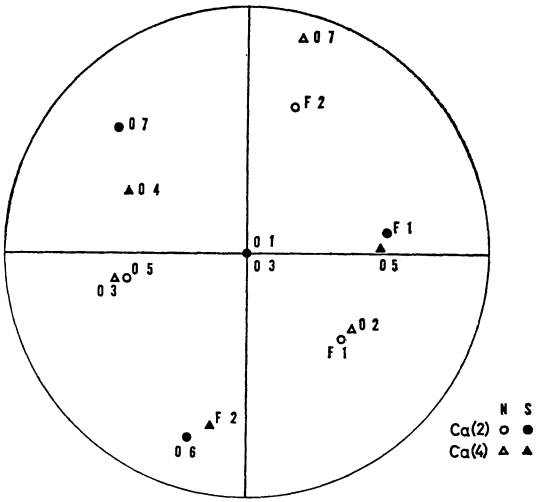

Fig. 4. Stereographic projection of the seven coordinated Ca polyhedra. Circles represent the oxygen atoms around Ca (2) and triangles correspond to those of Ca (4).

which corresponds to that of a seven coordinated face centered octahedral polyhedron. The total value is considered to decrease as the distortion of the polyhedron becomes large. Accordingly, the deviation from ideal form is considered to be greater in the case of Ca (4) than in Ca (2).

The coordination polyhedra of each calcium atoms form the columns parallel to the *a*-axis, and these columns are connected by sharing edges to construct the three-dimensional networks.

Fig. 5 illustrates the length of all the edges of Ca polyhedra. The regions A correspond to unshared edges of Ca (2), Ca (3) and Ca (4). In Ca (1), all the edges are shared. The regions B correspond to the edges shared with other Ca polyhedra, and the regions C also to the edges shared with Si–O tetrahedra. The mean values are A: 3.613 Å, B: 3.017 Å and C: 2.569 Å, and each value has 0.5 Å of difference. This fact can be explained by apply-

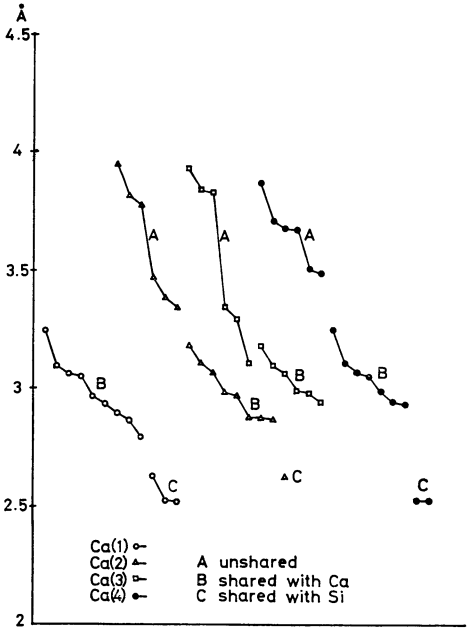

Fig. 5. The length of all the edges of Ca polyhedra are drawn. The length of abscissa has no meaning, only extended to show the four kinds of relations clearly.

ing an extended third rule by Pauling (Kamb, 1968).

In the linked tetrahedra, Si_2O_7, the bridging bonds Si (1)–O (1) and Si (2)–O (1) are significantly longer (1.658, 1.659 Å) than non-bridging bonds (average 1.606 Å). Fig. 6, originally drawn by Louisnathan and Smith (1970), shows the relation between Si–O–Si bridging angles and the Δd. The Δd means the difference between values of bridging and non-bridging Si–O distances. Those of cuspidine and rankinite (Saburi *et al.*, 1976) are newly plotted. The angle of Si (1)–O (1)–Si (2), 155.4°, is very close to that of tilleyite, 157.3° (Louisnathan and Smith, 1970). The values of Δd become smaller as the Si–O–Si angles increase (Cruickshank, 1961).

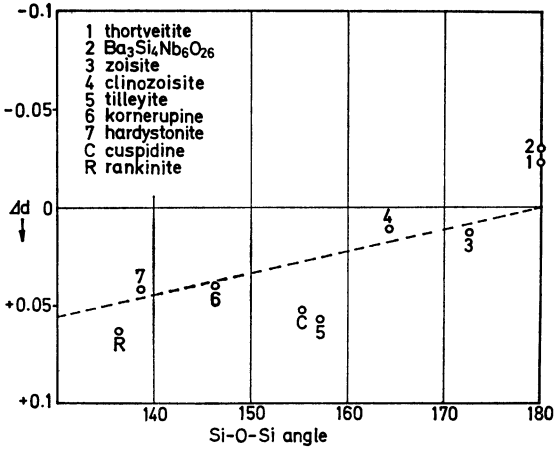

Fig. 6. The relation between Si-O-Si bridging angles and the Δd originally drawn by Louisnathan and Smith (1970). The Δd represents the difference between mean values of bridging and non-bridging Si-O distances. Those of cuspidine and rankinite (Saburi *et al.*, 1976) are newly plotted.

According to the work by Smirnova *et al.* (1955), the coordination numbers of all the calcium atoms were considered to be six. However, this consideration seems to be not correct. The coordination numbers of Ca (1), Ca (2), Ca (3) and Ca (4) are considered to be eight, seven, six and seven, respectively by this study.

The authors are much indebted to Professor K. Henmi, Okayama University, for his interest during their work. The intensity data were collected in the laboratory of Professor S. Sugiura, Kanazawa University.

REFERENCES

CRUICKSHANK, D. W. J. (1961) *Journ. Chem. Soc.*, 5486.
HENMI, K., KUSACHI, I. & HENMI, C. (1975) *Journ. Miner. Soc. Japan*, 12, 205.
KAMB, B. (1968) *Amer. Miner.*, 53, 1439.
LOUISNATHAN, S. J. & SMITH, J. V. (1970) *Zeits. Krist.*, 132, 288.

NUMANO, T., KUSACHI, I. & HANAZAWA, M. (1976) *Bull., School Educ. Okayama Univ.*, **45**, 47.

SABURI, S., KUSACHI, I., HENMI, C., KAWAHARA, A., HENMI, K. & KAWADA, I. (1976) *Miner. Journ.*, **8**, 240.

SAKURAI, T., ed. (1971) *Universal Crystallographic Computation Program System*, Cryst. Soc. Japan.

SMIRNOVA, R.F., RUMANOVA, I.M. & BELOV, N.V. (1955) *Zapiski Vsesoyuz. Miner. Obshchestva*, **84**, 159 (cited from Chemical Abstract).

Received July 24, 1976.