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Refinement of the structure of rankinite.

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ABSTRACT

The crystal structure of rankinite ($Ca_3Si_2O_7$) was refined to an R value of 0.033 by full matrix least-squares using 1492 three-dimensional counter-measured intensity data. The crystal is monoclinic, $P2_1/a$, with $a=10.557$ (1) Å, $b=8.885(3)$ Å, $c=7.858(1)$ Å, $\beta=119.586(6)°$, $Z=4$. The coordination polyhedra of calcium atoms form sheeets parallel to the (010) plane, between which Si_2O_7 groups are inserted. The lengths of Si-O bridge bonds are longer than those of non-bridge bonds. Listings are given of newly obtained bond lengths and bond angles of the structures.

Introduction

The crystal structure of rankinite ($Ca_3Si_2O_7$) was determined by Kusachi *et al.* (1975). There are in the structure arrays of Si_2O_7 groups parallel to the c-axis; the groups are linked together by Ca atoms each having seven coordinated oxygen atoms. The structural relationship between rankinite and kilchoanite ($Ca_6(SiO_4)(Si_3O_{10})$), the dimorphous form of rankinite, was also discussed. As their final residual was 11.6%, more exact parameters of atoms have been desired.

In the present paper, the results are reported of a refinement of the rankinite structure based on the counter-measured intensity data. More exact values of interatomic distances and angles have been obtained.

Throughout the investigation, the calculations were made on the computer NEAC 2200/500 at Okayama University and also HITAC 8800/8700 at the University of Tokyo.

Experimental and the refinement of the structure

The specimen used in this work was obtained from the spurrite-gehlenite skarn in Fuka, Okayama Prefecture, Japan (Henmi *et al.*, 1975).

The intensities of the reflections were measured on a Rigaku automated four-circle diffractometer using the 2θ-ω scan technique and MoKα radiation (λ=0.71069 Å) with a graphite monochromator. A crystal with approximate dimensions of 0.1×0.12 mm was mounted with the c-axis approximately parallel to the ϕ-axis of the diffractometer. Of a total of 1559 intensities measured up to 2θ=56°, 1492 had values bigger than 3σ. The integrated intensities were converted to structure factors by applying the Lorentz-polarization corrections. The spherical absorption correction was made.

The chemical formula and other crystal data such as unit cell dimensions and their standard deviations measured by the same diffractometer are shown in Table 1.

The parameters of all atoms determined by the previous work

Table 1. Crystallographic data of rankinite. Revised cell dimensions are given.

Chemical formula	$Ca_3Si_2O_7$
Space group	$P2_1/a$
Cell dimensions	a=10.557(1) Å
	b=8.885(3) Å
	c=7.858(1) Å
	β=119.586(6)°
Density	D_m=2.94, D_x=2.99 g/cm^3
Linear absorption coefficient	μ=28.1 cm^{-1} (for MoKα)

Table 2. Final positional parameters, anisotropic temperature factors with standard deviations in parentheses.

Atoms	x	y	z	$B11$	$B22$	$B33$	$B12$	$B31$	$B23$
Ca 1	.00867(11)	.05871(13)	.28957(16)	.00664(13)	.00860(15)	.01570(26)	−.00063(11)	.00473(15)	−.00055(16)
Ca 2	.16829(11)	.57424(12)	.20934(15)	.00611(12)	.00768(14)	.01390(24)	−.00001(10)	.00414(14)	−.00035(14)
Ca 3	.34078(11)	.90736(12)	.28490(16)	.00631(12)	.00782(14)	.01437(25)	.00015(10)	.00436(14)	.00025(15)
Si 1	.09055(15)	.21502(16)	.98429(21)	.00636(16)	.00756(18)	.01362(32)	−.00011(14)	.00424(19)	−.00014(20)
Si 2	.29602(15)	.23395(16)	.43206(21)	.00610(16)	.00751(18)	.01359(32)	−.00007(14)	.00397(18)	.00006(19)
O 1	.35625(36)	.39730(39)	.42113(50)	.00701(42)	.00791(48)	.01466(82)	.00034(37)	.00442(49)	.00034(51)
O 2	.17948(36)	.23873(41)	.50723(52)	.00670(42)	.00891(49)	.01590(85)	.00006(37)	.00496(50)	−.00009(53)
O 3	.40989(36)	.10295(41)	.54763(52)	.00680(42)	.00866(50)	.01582(84)	.00022(37)	.00448(50)	.00094(53)
O 4	.20191(37)	.15519(39)	.20980(52)	.00793(44)	.00732(47)	.01578(84)	−.00019(37)	·00504(51)	−.00012(51)
O 5	.09903(37)	.39489(40)	.97373(52)	.00702(43)	.00796(48)	.01563(85)	−.00005(37)	.00397(50)	−.00011(52)
O 6	.14429(36)	.14102(41)	.84624(51)	.00682(42)	.00862(50)	.01552(84)	.00030(37)	.00441(50)	−.00039(52)
O 7	.92820(37)	.16241(41)	.93207(56)	.00712(43)	.00804(49)	.02042(95)	.00007(38)	.00555(54)	.00097(56)

Table 3. Root-mean-square displacements of atoms along the principal axes of the vibration ellipsoids and direction cosine of these axes with respect to the crystallographic axes.

Atom	B_{isotr}	Axes	B	$\sqrt{\bar{u}^2}$	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
Ca 1	2.67	1	2.16	0.165	0.857	0.339	0.389
		2	2.78	0.188	0.386	−0.921	−0.047
		3	3.07	0.197	0.343	0.190	−0.920
Ca 2	2.40	1	2.05	0.161	−0.887	0.001	−0.461
		2	2.39	0.174	0.123	−0.963	−0.239
		3	2.76	0.187	−0.444	−0.269	0.854
Ca 3	2.47	1	2.12	0.164	−0.892	0.130	−0.432
		2	2.47	0.177	−0.174	−0.983	0.063
		3	2.82	0.189	−0.417	0.131	0.899
Si 1	2.40	1	2.15	0.165	−0.864	−0.143	−0.483
		2	2.36	0.173	0.014	−0.994	0.110
		3	2.73	0.186	0.523	−0.087	−0.848
Si 2	2.38	1	2.05	0.161	0.852	0.069	0.518
		2	2.36	0.173	0.014	−0.994	0.110
		3	2.73	0.186	0.523	−0.087	−0.848
O 1	2.59	1	2.28	0.170	0.697	−0.486	0.527
		2	2.56	0.180	−0.419	−0.873	−0.251
		3	2.94	0.193	0.582	−0.045	−0.812
O 2	2.70	1	2.23	0.168	−0.945	0.044	−0.324
		2	2.82	0.189	0.000	−0.991	−0.136
		3	3.06	0.197	−0.327	−0.128	0.936
O 3	2.72	1	2.28	0.170	−0.829	0.180	−0.529
		2	2.64	0.183	−0.351	−0.905	0.242
		3	3.25	0.203	−0.435	0.386	0.813
O 4	2.70	1	2.31	0.171	0.139	0.986	0.091
		2	2.67	0.184	0.778	−0.166	0.607
		3	3.13	0.199	0.613	−0.013	−0.790
O 5	2.73	1	2.34	0.172	0.751	0.107	0.652
		2	2.50	0.178	0.094	−0.994	0.054
		3	3.35	0.206	0.653	0.021	−0.757
O 6	2.71	1	2.28	0.170	0.851	−0.217	0.478
		2	2.67	0.184	−0.005	−0.914	−0.405
		3	3.19	0.201	0.525	0.343	−0.779
O 7	2.98	1	2.36	0.173	0.917	0.247	0.315
		2	2.50	0.178	0.173	−0.954	0.245
		3	4.07	0.227	0.361	−0.171	−0.917

(Kusachi *et al.*, 1975) were refined to $R=0.033$ by full-matrix least squares. The final atomic parameters and anisotropic temperature factors are shown in Table 2. Table 3 shows the root-mean-squared displacement of the atoms along the principal axes of the vibration ellipsoids and direction cosine of these axes with respect to the crystallographic axes.

Discussion

The structure of rankinite determined by film methods was discussed in detail in the previous investigation (Kusachi *et al.*, 1975). In this report, revised interatomic distances from silicon or calcium to oxygen atoms are discussed briefly.

The Si_2O_7 groups are situated among seven coordinated calcium atoms. Si-O distances are in the range from 1.593 to 1.677 Å (Table 4a). In the Si_2O_7 groups, the lengths of Si-O bridge bonds are signi-

Table 4a. The interatomic distances calculated.

Si(1)	-O(4)*	1.658(3)Å	Ca(2)	-O(1)	2.433(3)Å
	-O(5)	1.605(4)		-O(2)	2.479(3)
	-O(6)	1.593(5)		-O(3)	2.439(5)
	-O(7)	1.622(4)		-O(5)	2.273(4)
Si(2)	-O(1)	1.604(4)Å		-O(5′)	2.470(4)
	-O(2)	1.607(5)		-O(6)	2.305(5)
	-O(3)	1.596(4)		-O(7)	2.575(4)
	-O(4)*	1.677(4)	Ca(3)	-O(2)	2.303(4)Å
Ca(1)	-O(1)	2.461(3)Å		-O(3)	2.515(4)
	-O(1′)	2.335(5)		-O(3′)	2.291(3)
	-O(2)	2.385(3)		-O(4)	2.548(4)
	-O(4)	2.560(5)		-O(5)	2.413(5)
	-O(6)	2.279(4)		-O(6)	2.617(4)
	-O(7)	2.666(4)		-O(7)	2.564(3)
	-O(7′)	2.913(5)			

* bridging bonds

Table 4b. The interatomic angles calculated.

O(4)-Si(1)-	-O(5)	110.3(2)°	O(1)-Ca(2)-	-O(6)	79.0(1)°
O(4)-	-O(6)	107.0(2)	O(1)-	-O(7)	153.9(1)
O(4)-	-O(7)	106.3(2)	O(2)-	-O(3)	63.6(1)
O(5)-	-O(6)	109.1(2)	O(2)-	-O(5)	161.9(1)
O(5)-	-O(7)	110.7(2)	O(2)-	-O(5′)	120.4(1)
O(6)-	-O(7)	113.3(2)	O(2)-	-O(6)	77.4(1)
O(1)-Si(2)-	-O(2)	113.1(2)°	O(2)-	-O(7)	78.2(1)
O(1)-	-O(3)	118.9(2)	O(3)-	-O(5)	127.9(2)
O(1)-	-O(4)	111.6(2)	O(3)-	-O(5′)	73.3(1)
O(2)-	-O(3)	108.0(2)	O(3)-	-O(6)	140.9(1)
O(2)-	-O(4)	103.1(2)	O(3)-	-O(7)	91.6(1)
O(3)-	-O(4)	100.4(2)	O(5)-	-O(5′)	77.8(1)
Si(1)-O(4)-	-Si(2)	136.2(2)°	O(5)-	-O(6)	89.3(2)
O(1)-Ca(1)-	-O(1′)	84.3(1)°	O(5)-	-O(7)	112.7(1)
O(1)-	-O(2)	80.8(1)	O(5′)-	-O(6)	134.6(1)
O(1)-	-O(4)	104.7(1)	O(5′)-	-O(7)	63.4(1)
O(1)-	-O(6)	86.1(1)	O(6)-	-O(7)	83.0(1)
O(1)-	-O(7)	155.9(2)	O(2)-Ca(3)-	-O(3)	87.6(1)°
O(1)-	-O(7′)	87.7(1)	O(2)-	-O(3′)	92.8(1)
O(1′)-	-O(2)	90.7(1)	O(2)-	-O(4)	118.8(2)
O(1′)-	-O(4)	149.2(1)	O(2)-	-O(5)	136.3(1)
O(1′)-	-O(6)	81.6(1)	O(2)-	-O(6)	74.7(1)
O(1′)-	-O(7)	118.6(1)	O(2)-	-O(7)	81.6(1)
O(1′)-	-O(7′)	142.1(1)	O(3)-	-O(3′)	76.7(1)
O(2)-	-O(4)	62.6(1)	O(3)-	-O(4)	59.6(1)
O(2)-	-O(6)	165.4(2)	O(3)-	-O(5)	129.3(1)
O(2)-	-O(7)	105.0(1)	O(3)-	-O(6)	154.0(1)
O(2)-	-O(7′)	124.5(1)	O(3)-	-O(7)	119.3(1)
O(4)-	-O(6)	127.7(2)	O(3′)-	-O(4)	122.3(1)
O(4)-	-O(7)	60.3(1)	O(3′)-	-O(5)	77.1(1)
O(4)-	-O(7′)	68.5(1)	O(3′)-	-O(6)	85.1(1)
O(6)-	-O(7)	89.6(1)	O(3′)-	-O(7)	162.5(1)
O(6)-	-O(7′)	60.9(1)	O(4)-	-O(5)	101.8(1)
O(7)-	-O(7′)	69.6(1)	O(4)-	-O(6)	146.1(1)
O(1)-Ca(2)-	-O(2)	79.5(1)°	O(4)-	-O(7)	74.5(1)
O(1)-	-O(3)	90.5(1)	O(5)-	-O(6)	62.2(1)
O(1)-	-O(5)	86.0(1)	O(5)-	-O(7)	95.4(1)
O(1)-	-O(5′)	141.4(1)	O(6)-	-O(7)	77.4(1)

ficantly longer than those of nonbridge bonds (Table 4a), the mean values corresponding to 1.668 and 1.605 Å respectively. These facts are consistent with the d-p π-bond model for silicates (Cruickshank, 1961).

All calcium atoms, Ca(1), Ca(2) and Ca(3), have seven nearest neighbours of oxygen atoms. Each coordination polyhedron forms the shape of a distorted decahedron, but there is a regularity in the model of distortion among these three decahedrons.

The interatomic angles calculated are shown in Table 4b.

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