

The structure of rankinite

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ABSTRACT

The crystal structure of rankinite has been determined by Patterson and direct methods and refined to $R=11.6\%$, using a crystal from Fuka, Bitchu-cho, Japan: $P2_1/a$, a 10.60(2), b 8.92(2), c 7.89(2) Å, β 119.6(1)°, $Z=4$ $\text{Ca}_3\text{Si}_2\text{O}_7$. There are in the structure arrays of Si_2O_7 groups parallel to the c axis, and the groups are linked together by Ca's each having seven near oxygen atoms: the Ca-O bond length in the structure is in the range from 2.25 to 2.90 Å. Si-O is from 1.52 to 1.65 Å. The structural relationships between rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) and kilchoanite [$\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$] are described briefly.

Introduction

Rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) is considered to be dimorphous to kilchoanite [$\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$], and its lattice dimensions were determined by Moody (1953), but its crystal structure has not been determined. On the other hand, Roy, Gard, Nicol and Taylor (1960) described the lattice dimensions of kilchoanite, which were refined by Agrell and Gay (1961). The crystal structure of kilchoanite was determined by Taylor (1971) but the structural relationship between these two di-

morphous minerals was not discussed, because of the lack of the data on the structure of rankinite.

In the present paper, the result of the crystal structure determination of rankinite by three dimensional intensity data is given and the structural relationship between rankinite and kilchoanite is also discussed. The specimen used in this investigation was found from Fuka, Bitchu-cho, Okayama Pref., Japan. It occurs as a minor component of gehlenite-spurrite skarns. General descriptions of this mineral were reported by Henmi *et al.* (1975).

Experimental

A small crystal having approximately the shape of a sphere ($r=0.1$ mm) was cautiously obtained under the polarizing microscope. The glass fibres of about 0.02 mm dimensions were used to mount the specimen using colourless nail-enamel as adhesive agent. The oscillation as well as the Weissenberg photographs were taken about a -, b - and c -axis. The lattice constants were derived by Weissenberg methods using the standard material of metal silicon powder ($a=5.4306\text{\AA}$) and refined by least-squares calculations (Christ, 1956). The crystallographic data obtained are as follows :

$$\begin{aligned} & \text{Monoclinic,} & P2_1/a \\ & a=10.60\pm 0.02 \text{\AA} \\ & b= 8.92\pm 0.02 \text{\AA} \\ & c= 7.89\pm 0.02 \text{\AA} \\ & \beta=119.6^\circ \pm 0.1^\circ \\ & D=2.97 \text{ g/cm}^3, \quad Z=4 \end{aligned}$$

The lattice constants obtained agree with the result by the previous author.

The intensity was measured visually by multi-film methods, and Lorenz and Polarization corrections were made in the usual way. No absorption corrections were made because of the very small size of

the specimen. The structure was investigated based on 840 non zero reflections. From the three dimensional intensity data thus obtained, Patterson syntheses were made and the positions of three independent Ca atoms were found in the map. Next, the authors tried to find the positions of silicon atoms according to the $(F_o - F_c)$ Fourier maps with the phases given by Ca atoms. But it was difficult to find these peaks uniquely. Accordingly, the symbolic addition method was partly adopted. The 185 reflections more than $E=1.50$ were calculated from the 840 non zero reflections using the program Sigma II made by T. Ashida, Osaka University (Ashida, 1973). Next, the symbolic phases A, B and C were added to the 36 reflections more than $E=2.00$, and eight possibilities were checked by the program tangent formula made by T. Ashida (Ashida, 1973). One of the eight sets of signs was found to give R (Karle)=0.24. The E -map based on the set of signs revealed positions of calcium atoms consistent with those from the Patterson syntheses. The positions of Si atoms were then found from the peaks of the E -map and also from $(F_o - F_c)$ Fourier maps with the phases given by Ca atoms. Finally, the positions of oxygen atoms were found by $(F_o - F_c)$ Fourier maps with phases given by Ca and Si atoms. Then the parameters of all atoms determined by both Patterson and direct methods were refined with diagonal least-squares program (Sakurai, 1971) and the residual R was reduced to 19%. Then the block diagonal least-squares program was used to refine the parameters more correctly. After ten cycles of refinement, $R=11.6\%$ was obtained.

The atomic parameters obtained are shown in Table 1, and inter-atomic distances and angles calculated from these parameters are also tabulated in Table 2.

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

Table 1. The atomic parameters of rankinite refined after ten cycles of least-squares refinement. The standard deviations of atomic parameters in parentheses.

	X	Y	Z	$B(\text{\AA}^2)$
Ca1	0.0071(3)	0.0552(3)	0.2893(4)	1.46
Ca2	0.1677(3)	0.5745(3)	0.2083(4)	1.42
Ca3	0.3403(3)	0.9034(3)	0.2839(4)	1.41
Si1	0.2948(4)	0.2357(4)	0.4314(5)	1.10
Si2	0.0903(4)	0.2145(4)	0.9843(5)	0.95
O1	0.3579(10)	0.4038(10)	0.4229(13)	0.89
O2	0.1782(10)	0.2344(10)	0.5033(13)	1.12
O3	0.4105(10)	0.1016(10)	0.5523(13)	0.78
O4	0.2007(10)	0.1629(10)	0.2120(13)	0.63
O5	0.0970(10)	0.3857(10)	0.9810(13)	0.51
O6	0.1451(10)	0.1487(10)	0.8437(13)	0.55
O7	0.9299(10)	0.1536(10)	0.9394(14)	0.17

Results and discussion

The schema of the structure thus obtained is shown in Fig. 1(a) and (b). Fig. 1(a) shows the projection parallel to the b -axis, and Fig. 1(b) is that of c -axis. In Fig. 1(a) and (b), the small single, the large single and large double circles correspond to silicon, oxygen, and calcium atoms respectively. The numerals written on atoms represent the height of each atom. In the structure of rankinite, two silicon-oxygen tetrahedra are linked to form a unit (Si_2O_7), and three kinds of calcium atoms have all seven nearest neighbours of oxygen atoms. The interatomic distances between Ca and O have the values from 2.25 to 2.90 Å. The angles O-Ca-O are all from 60 to 87 degrees. The Si_2O_7 groups have shapes of nearly regular tetrahedra like other silicates, and the distances between Si-O are in the range from 1.52 to 1.65 Å, also the angles of O-Si-O is from 106° to 115°. This value is larger than Si_2O_7 tetrahedra of other silicates. These results are shown in Table 2.

Table 2. The interatomic distances and angles calculated.

Ca1-O1	2.31(2) Å	O1-Ca1-O1'	83.0(1.5)°
-O1'	2.39(2)	O2-Ca1-O4	60.4(1.5)
-O2	2.36(2)	O7-Ca1-O7'	66.7(1.5)
-O4	2.58(2)	O6-Ca1-O1	81.4(1.5)
-O6	2.29(2)		
-O7	2.88(2)		
-O7'	2.59(2)		
Ca2-O1	2.40(2) Å	O2-Ca2-O3	63.5(1.5)°
-O2	2.46(2)	O1-Ca2-O5	85.2(1.5)
-O3	2.41(2)	O5'-Ca2-O7	61.8(1.5)
-O5	2.28(2)	O2-Ca2-O6	76.7(1.5)
-O5'	2.44(2)		
-O6	2.30(2)		
-O7	2.65(2)		
Ca3-O2	2.32(2) Å	O2-Ca3-O3	86.9(1.5)°
-O3	2.27(2)	O5-Ca3-O3	75.8(1.5)
-O3'	2.55(2)		
-O4	2.63(2)		
-O5	2.48(2)		
-O6	2.51(2)		
-O7	2.53(2)		
Si1-O1	1.65(2) Å	O1-Si1-O2	114.9(1.6)°
-O2	1.59(2)	O1-Si1-O3	119.1(1.6)
-O3	1.63(2)	O2-Si1-O3	106.0(1.6)
-O4	1.63(2)		
Si2-O4	1.64(2) Å	O5-Si2-O6	108.6(1.6)°
-O5	1.52(2)	O5-Si2-O7	112.2(1.6)
-O6	1.59(2)	O6-Si2-O7	115.1(1.6)
-O7	1.64(2)		
		Si1-O4-Si2	140.1(1.6)°

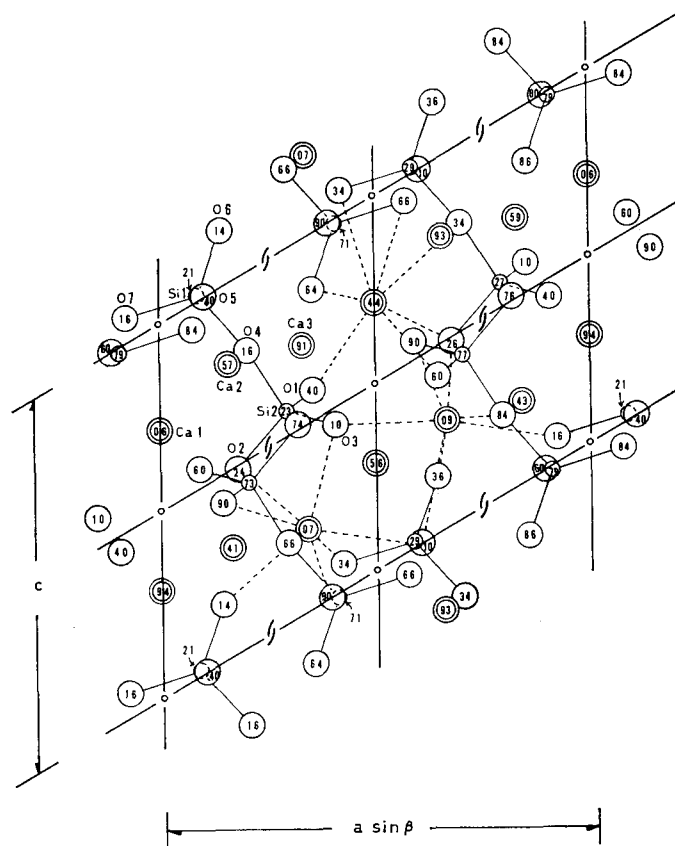


Fig. 1. Structure of rankinite. (a) Projection parallel to b . Large double circle, large single circle and small single circle represent calcium, oxygen and silicon atoms, respectively.

Both rankinite and kilchoanite have the experimental formula of $\text{Ca}_3\text{Si}_2\text{O}_7$, and are said to be dimorphous to each other. In Fuka district, the rankinite crystals of the diameter of 0.2-1 mm are frequently surrounded by kilchoanite crystals with similar dimensions. The latter may be considered as lower temperature form of the

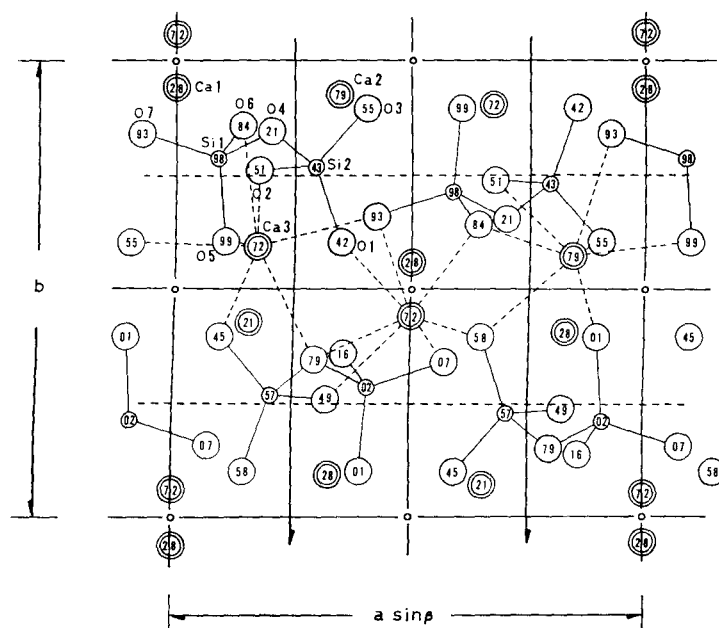


Fig. 1. Structure of rankinite. (b) Projection parallel to c .

former. According to Roy (1958), their equilibrium boundary lies on 810°C at 2,000 psi and 825°C at 21,000 psi water pressure. It would be worthwhile to discuss the structural relationship between these two minerals.

The lattice dimensions and other crystal data of these two minerals are as follows:

Rankinite	Kilchoanite
$\text{Ca}_3\text{Si}_2\text{O}_7$	$\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$
$a=10.60 \text{ \AA}$	$a=11.45 \text{ \AA}$
$b=8.92 \text{ \AA}$	$b=5.08 \text{ \AA}$
$c=7.89 \text{ \AA}$	$c=22.05 \text{ \AA}$
$\beta=119.6^{\circ}$	
monoclinic	orthorhombic
space group $P2_1/a$	space group $I2cm$

As for lattice dimensions, there are apparently no clear relationships between them. However, our structure analysis of rankinite has now made it possible to discuss the structural relationships between these two minerals.

As shown in Fig. 2, the Si_2O_7 linked tetrahedra are arranged parallel to the c -axis. The calcium atoms are placed among these linked tetrahedra. The figure written on each atom shows the height parallel to the projection. The calcium atoms of rankinite

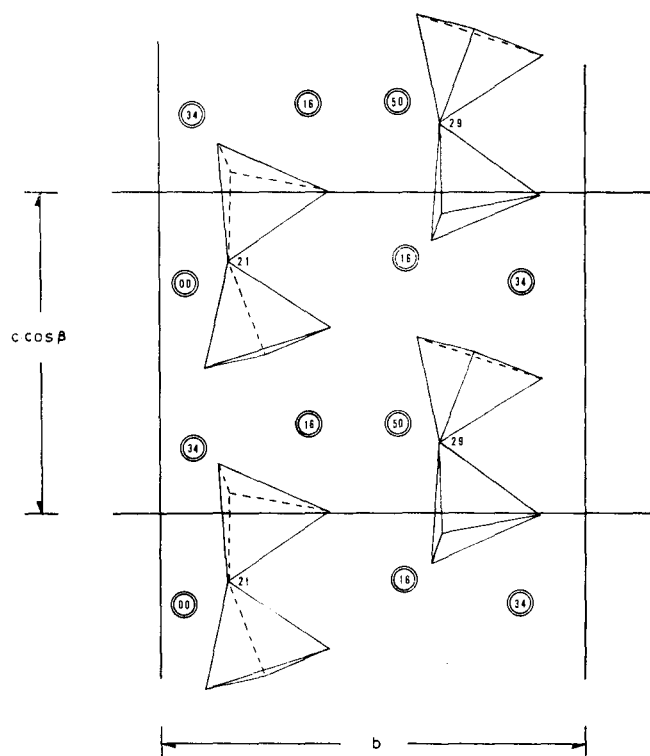


Fig. 2. The schema of the structure of rankinite parallel to a -axis. The double circles represent calcium atoms. In order to compare the structure with that of kilchoanite, Si_2O_7 groups are drawn as linked tetrahedra.

have seven nearest neighbours of oxygens.

The structure of kilchoanite, based on the results of Taylor (1971), is shown in Fig. 3. Kilchoanite contains isolated SiO_4 tetrahedra and Si_3O_{10} triple linked tetrahedra. There are four kinds of calcium atoms in kilchoanite, and one of them has eight nearest neighbours of oxygen, and the other three are octahedrally coordinated.

In Fig. 3, if tetrahedra B will be cut off from tetrahedra A, and linked to tetrahedra C, then all the linked tetrahedra are arranged

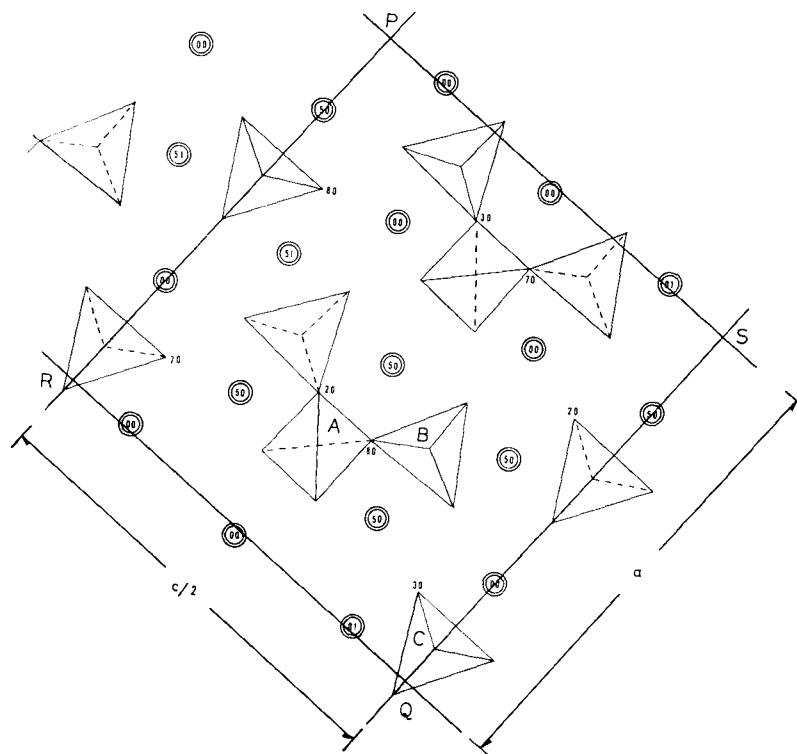


Fig. 3. The structure of kilchoanite schematically represented. The double circles correspond to calcium atoms and the numerals mean the height of each point.

to the direction $\bar{a}+\bar{c}/2$, and become similar to the rankinite structure. PRQS square shows the half of the unit cell. The length of PQ/2, as it were, the half length of $\bar{a}+\bar{c}/2$ of kilchoanite is almost equal to the c length of rankinite. Accordingly, there are intimate structural and directional relationships between rankinite and kilchoanite. But in natural specimens in Fuka district, there are no clear directional relations between these two minerals (Henmi *et al.*, 1975).

Also, in order to find more exact parameters of atoms in the structure, the counter method is desirable. The authors are trying to find larger specimens fitting for automated four-circle diffractometer.

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