MEMOIRS OF THE COLLEGE OF SCIENCE, UNIVERSITY OF KYOTO, SERIES B,
Vol. XXII, No. 2, Article 2, 1955.

The Crystal Structure of Allanite, $OH(Ca, Ce)_2 (Fe^{III}, Fe^{II}) Al_2O Si_2O_7SiO_4$

By

Tateo UEDA

Geological and Mineralogical Institute, University of Kyoto

(Received Sept. 21, 1955)

Abstract

The crystal structure of allanite is the same as that of epidote. Taking the structural aspect as well as the results of the chemical analyses into consideration, $OH\,(Ca, Ce)_2\,(Fe^{III}, Fe^{II})\,Al_2\,O\,Si_2\,O_7\,SiO_4$ is given to the mineral as its chemical formula.

Introduction

Allanite, though a common mineral, has not yet been found in its crystal structure. As it bears, however, a close resemblance to epidote in the crystal form, axial ratio and chemical constitution, although the chemical formula of allanite is not yet fully established, the structure of allanite may be the same as that of epidote or at least the two minerals must be in close relationship to each other in their structures. It will, therefore, be interesting to inquire into the structural relationship between these two minerals. The crystal structure of epidote has been analysed by ITO[1] and his coworkers. As for allanite, even its chemical formula is not yet fully established as said above. The following is the formulae given to the mineral by several authors.

DANA[2]	$HR_2^{II}R_3^{III}Si_3O_{13}$ where R^{II}: Ca, Fe^{II}; R^{III}: Al, Fe^{III}, Ce, Di, La, Y
CORRENS[3]	$(Ca, Ce, La, Na)_2\,(Al, Fe, Be, Mg, Mn)_3\,[OH \mid (SiO_4)_3]$?
KRAUS, HUNT & RAMSDELL[4]	$Ca_2\,(Al, Ce, Fe)_3\,OH\,(SiO_4)_3$
WINCHELL[5]	$(Ca, Ce, La)_2\,(Al, Fe^{III}, Fe^{II})_3\,(OH)\,Si_3\,O_{12}$
HILLER[6]	$(Ca, Ce)_2\,(Al, Fe^{III}, Mg, Fe^{II})_3\,[Si_3O_{12} \mid (OH)]$
MACHATSCHKI[7]	$(OH, F)\,(Ca, Ce, usw., Na, Th, U)_2\,(Al, Fe, Mg, Ti, Mn)_2\,(Si, P, Be, Al)_4\,O_{12}$

The structure analysis will, therefore, be begun with the establishment of a more suitable formula for the mineral.

Establishment of the chemical formula

Specimens found in biotite granite at Daimonji-yama, Kyoto Pref., Japan were chemically analysed. They were slender, needle-like in shape and a large majority of them was about 2 to 5 mm in length and about 1 mm in diameter. More than twenty pieces of them were crushed together into powder and submitted to chemical analysis. Result obtained is shown in Table 1.

Table 1

Components	Weight percentages	Numerical ratios of the atoms	
		Cation	Oxygen
SiO_2	30.54	0.508	1.017
Al_2O_3	17.48	0.343	0.515
Fe_2O_3	4.19	0.052	0.079
FeO	9.22	0.128	0.128
CaO	11.00	0.196	0.196
MgO	0.85	0.021	0.021
MnO	0.58	0.008	0.008
ThO_2	1.27	0.005	0.010
Ce_2O_3	9.94	0.061	0.091
$[Ce]_2O_3$	10.55	0.063	0.094
$[Y]_2O_3$	0.63	0.005	0.007
TiO_2	1.10	0.014	0.028
SnO_2	0.41	0.003	0.005
$H_2O^{(+)}$	1.59	0.176	0.088
$H_2O^{(-)}$	0.88		
Total	100.23		2.287

From the result of the chemical analysis the writer has derived chemical formula for allanite as follows:

$$H_{176}\ Ca_{196}\ Mg_{21}\ Fe^{III}_{52}\ Fe^{II}_{128}\ Th_5\ Ce_{61}\ [Ce]_{63}\ [Y]_5\ Al_{343}\ Mn_8\ Sn_3\ Si_{508}\ Ti_{14}\ O_{2287}$$
$$= H_{1.0}\ (Ca,\ Mg)_{1.2}\ Fe^{III}_{0.3}\ Fe^{II}_{0.7}\ (Th,\ Ce,\ [Ce],\ [Y])_{0.8}\ Al_{1.9}\ Mn_{0.1}\ Si_{2.9}\ Ti_{0.1}\ O_{13.0}$$

Having Ca represent $(Ca,\ Mg)$ and Ce represent $(Th,\ Ce,\ [Ce],\ [Y])$,

$$= H_{1.0}\ Ca_{1.2}\ Fe^{III}_{0.3}\ Fe^{II}_{0.7}\ Ce_{0.8}\ Al_{2.0}\ Si_{3.0}\ O_{13.0}.$$

Conceiving that a part of Ca atoms has been replaced by Ce atoms and because of neutralization a part of Fe^{III} atoms has been replaced by Fe^{II} atoms just as many as Ca atoms by Ce atoms, the writer has finally obtained the chemical formula for allanite as follows:

$$H\ (Ca,\ Ce)_2\ (Fe^{III},\ Fe^{II})\ Al_2\ Si_3\ O_{13}.$$

The above formula suggests that allanite is in its chemical constitution nothing else than epidote, whose chemical formula is $H\,Ca_2\,Fe\,Al_2\,Si_3\,O_{13}$, in which Fe^{III}

atoms have been replaced by Fe^{II} atoms just as many as Ca atoms by Ce atoms. To examine whether the suggestion is true or not, the writer has referred to some other results of the chemical analyses of allanite found in Japan, Korea and Manchuria. These specimens were totally analysed in the writer's laboratory by the writer and his fellows. From the weight percentages of the components have been calculated numerical ratios of the atoms, as shown in Table 2, from which those of *Si*, *Al*, *Mn*, *Ti*, *Sn* and *H* are excluded.

Table 2

Localities	Numerical ratios of the atoms							
	Fe^{III}	Fe^{II}	*Ca*	*Mg*	*Th*	*Ce*	[*Ce*]	[*Y*]
Mie-mura (Japan)	.106	.141	.173	.001	.005	.057	.059	.001
Hagata-mura (Japan) A	.036	.154	.184	.015	.007	.041	.065	.023
Hagata-mura (Japan) B	.034	.154	.183	.016	.007	.047	.059	.023
Kojima-mura (Japan)	.098	.147	.147	.003	.008	.045	.058	.041
Ôtsunagi-mura (Japan)	.090	.140	.129	.009	.005	.061	.064	.024
Nogizawa-mura (Japan)	.070	.140	.193	.012	.013	.046	.054	.016
Shûgakuin (Japan)	.052	.128	.196	.021	.005	.061	.063	.005
Kitayamato-mura (Japan)	.068	.147	.146	.003	.008	.037	.057	.051
Kido-mura (Japan)	.120	.120	.184	.015	.003	.044	.089	.001
Anak-ub (Korea) A	.024	.174	.179	.019	.002	.073	.067	.004
Anak-ub (Korea) B	.036	.139	.207	.023	.002	.065	.056	.007
Hakson-myon (Korea)	.088	.165	.193	.008	.001	.060	.066	.001
Santaikou (Manchuria)	.142	.077	.252	.021	.004	.041	.021	.014
Hsiayuhekou (Manchuria)	.120	.088	.330	.010	.012	.042	.019	.001

For these specimens are plotted the numerical ratios of $(Th+Ce+[Ce]+[Y])$ atoms to those of $(Ca+Mg)$ atoms in Fig. 1 and the numerical ratios of Fe^{II} atom to those of Fe^{III} atom in Fig. 2. In these figures are appreciable the general tendencies that $(Th+Ce+[Ce]+[Y])$ ratio decreases as $(Ca+Mg)$ ratio increases, likewise, Fe^{II} ratio decreases as Fe^{III} ratio increases. The numerical ratios of Fe^{II} atom are also plotted to those of $(Th+Ce+[Ce]+[Y])$ atoms in Fig. 3. In this case is appreciable the general tendency that Fe^{II} ratio increases as $(Th+Ce+[Ce]+[Y])$ ratio increases. These relations were, further, stochastically examined and the *t*-values have been found as high as 6.32, 3.55 and 4.66 respectively, between $(Th+Ce+[Ce]+[Y])$ ratios and $(Ca+Mg)$ ratios, between Fe^{II} ratios and Fe^{III} ratios, and between Fe^{II} ratios and $(Th+Ce+[Ce]+[Y])$ ratios. Accordingly, the relations are significant on the level of 0.1%, 1% and 0.1% respectively. As a matter of course it is concluded that, in allanite, $(Th+Ce+[Ce]+[Y])$ ratio decreases with the increase of $(Ca+Mg)$ ratio, Fe^{II} ratio decreases with that of Fe^{III} ratio and Fe^{II} ratio increases with the increase of $(Th+Ce+[Ce]+[Y])$ ratio. The chemical formula given above for allanite seems, therefore,

to be justifiable. The writer has adopted the formula for the structure analysis.

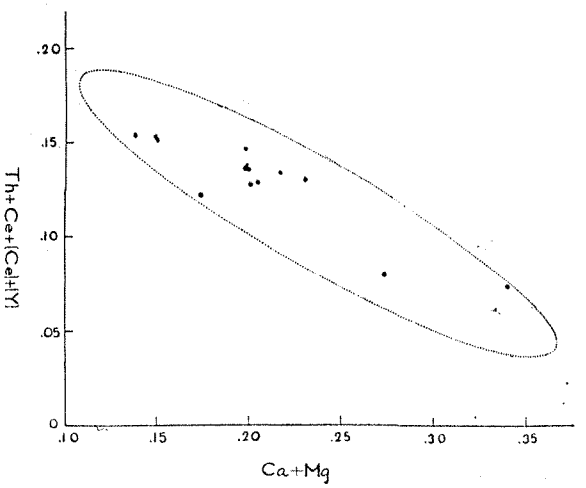

Fig. 1. Relation between the numerical ratios of $(Th+Ce+[Ce]+[Y])$ atoms and those of $(Ca+Mg)$ atoms.

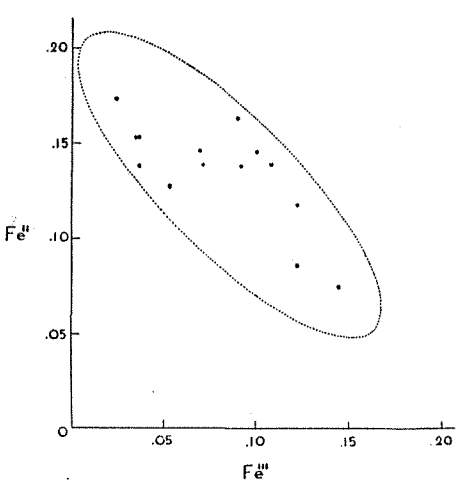

Fig. 2. Relation between the numerical ratios of Fe^{II} atom and those of Fe^{III} atom.

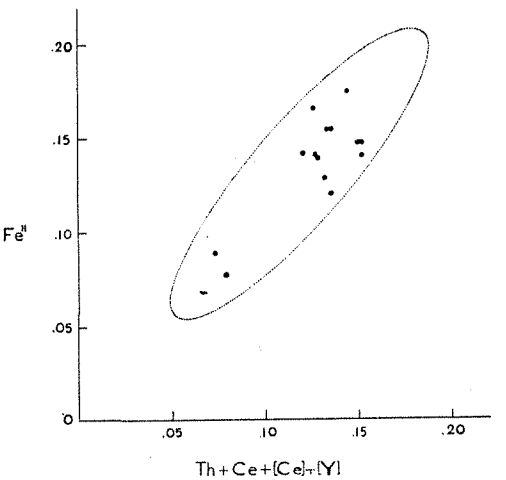

Fig. 3. Relation between the numerical ratios of Fe^{II} atom and those of $(Th+Ce+[Ce]+[Y])$ atoms.

Determinations of the cell-dimensions, cell-volume and the number of molecules

Specimens found at Daimonji-yama were used in X-ray spectrometry. A slender specimen, elongated parallel to the b-axis, about 3 mm in length and about 0.2 mm in diameter, was submitted to the b-axis rotation and oscillation photographing. For the a- and c-axis rotation and oscillation photographing, small rods parallel to the a-axis and c-axis respectively were cut out of somewhat large crystals. The rods were about 1.8 mm in length and about 0.2 mm in diameter. The X-ray spectrometry was carried out using Cu-$K\alpha$ radiation ($\lambda = 1.542$ Å) throughout. The cell-dimensions and cell-volume are as follows:

$$\begin{aligned} a &= 8.98 \pm 0.01 \text{ Å} \\ b &= 5.75 \pm 0.00 \text{ Å} \\ c &= 10.23 \pm 0.01 \text{ Å} \\ \beta &= 115°00' \pm 04' \\ V &= 479 \text{ Å}^3 \end{aligned}$$

giving the axial ratio $a : b : c = 1.562 : 1 : 1.779$, which is in good agreement with that given by DANA[8].

Molecular weight has been calculated as follows:

$$H_{1.0}\ Ca_{1.2}\ Fe^{III}_{0.3}\ Fe^{II}_{0.7}\ Ce_{0.8}\ Al_{2.0}\ Si_{3.0}\ O_{13.0}$$
$$= 1.01 + 48.10 + 16.75 + 39.09 + 112.10 + 53.94 + 84.18 + 208 = 563.17$$

The specific gravity measured by means of pycnometer method is 3.85. The number of molecules in a unit cell turns out as follows:

$$\frac{479 \times 3.85 \times 10^{-24}}{563 \times 1.66 \times 10^{-24}} = 1.97 \fallingdotseq 2$$

Then, $Z = 2$.

Structure analysis

Complete sets of oscillation photographs were taken with rotation about the a-, b- and c- axis to get all possible reflexions. The only possible space group for allanite is $C^2_{2h} - P2_1/m$, the reflexion $0k0$ being absent when k is odd. The intensities of reflexions on the oscillation photographs were estimated visually and converted into numerical values on an arbitrary scale. They were corrected for the polarization and Lorentz factors as usual, but not for absorption nor extinction. A set of numbers proportional to the structure factors have thus been obtained.

Similarity between allanite and epidote with respect to their chemical formulae and cell-dimensions, as well as identity of their space group and the number of molecules in a unit cell with each other suggest that coordinates for corresponding atoms in these two minerals might also be identical. In the space group of $C^2_{2h} - P2_1/m$, equivalent positions are as follows:

(a) 000; $0\ \frac{1}{2}\ 0$. (b) $\frac{1}{2}\ 0\ 0$; $\frac{1}{2}\ \frac{1}{2}\ 0$.

(c) $00\ \frac{1}{2}$; $0\ \frac{1}{2}\ \frac{1}{2}$. (d) $\frac{1}{2}\ 0\ \frac{1}{2}$; $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$.

(e) $\bar{x}\ \frac{1}{4}\ z$; $x\ \frac{3}{4}\ \bar{z}$.

(f) $x\ y\ z$; $\bar{x}\ \bar{y}\ \bar{z}$; $\bar{x},\ \frac{1}{2}+y,\ \bar{z}$; $x,\ \frac{1}{2}-y,\ z$.

In the case of the structure analysis for epidote, ITO[9] has put four *Al*-atoms in (a) and (c), three sets of four *O*-atoms in (f) and the rest in (e). In the present case the writer, assuming that the crystal structure of allanite might be the same as that of epidote, calculated structure factors for *h0l*, *0kl* and *hk0* reflexions with coordinates for atoms in epidote, substituting (Fe^{III}, Fe^{II}) for *Al* (*Fe*) and (*Ca*, *Ce*) for *Ca*.

The structure factor of *hkl* reflexion in a space group of $C_{2h}^2-P2_1/m$ runs:

$$F\ (hkl) = \Sigma\ 4\ f\ \cos\ 2\pi\ (hx+\frac{k}{4}+lz)\ \cos\ 2\pi\ (ky-\frac{k}{4}),$$

where f is the atomic scattering factor. The writer used for it the value given in the *Internationale Tabellen*. For the scattering factor of (*Ca*, *Ce*), the writer applied value obtained by adding three fifths of the value of *Ca* scattering factor to two fifths of the value of *Ce* scattering factor. Since, in the specimen found at Daimonji-yama the numerical ratio of *Ca* atoms to that of *Ce* atoms is 1.2 : 0.8 ($=3$: 2). The observed and calculated structure factors were in good agreement.

For the refining of the coordinates of the atoms, electron densities projected on (010) and (001) planes were evaluated by means of the Fourier syntheses with the calculated structure factors. Electron densty $\rho\ (x, z)$ at a point (x, z) projected on (010) plane runs:

$$\begin{aligned}\rho\ (x,z) = \frac{1}{A}\Big\{&F(000)+2\sum_h F(h00)\cos 2\pi\, h\,x+2\sum_l F(00l)\cos 2\pi\, l\,z\\&+2\sum_h\Big[\sum_l\Big\{F(h0l)+F(\bar{h}0l)\Big\}\cos 2\pi\, lz\Big]\cos 2\pi\, hx\\&-2\sum_h\Big[\sum_l\Big\{F(h0l)-F(\bar{h}0l)\Big\}\sin 2\pi\, lz\Big]\sin 2\pi\, hx\Big\},\end{aligned}$$

and electron density $\rho\ (x, y)$ at a point (x, y) projected on (001) plane:

$$\begin{aligned}\rho\ (x,y) = \frac{1}{A}\Big\{&F(000)+2\sum_h F(h00)\cos 2\pi\, h\,x+2\sum_k^{k=2n} F(0k0)\cos 2\pi\, k\,y\\&+4\sum_h\Big[\sum_k^{k=2n}\Big\{F(hk0)\cos 2\pi\, ky\Big\}\Big]\cos 2\pi\, hx\\&-4\sum_h\Big[\sum_k^{k=2n+1}\Big\{F(hk0)\sin 2\pi\, ky\Big\}\Big]\sin 2\pi\, hx\Big\}.\end{aligned}$$

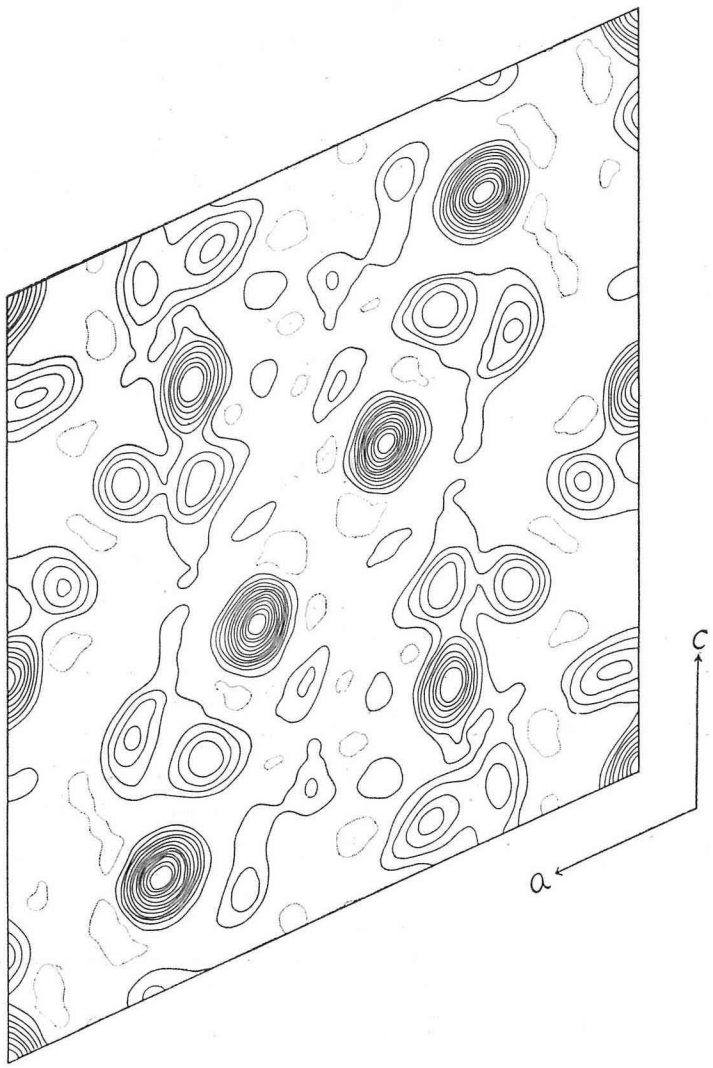

Fig. 4. Electron density projected on (010) plane.

The summations were carried out with the aid of Beevers and Lipson strips at the intervals of $a/_{60}$, $c/_{60}$; $a/_{60}$, $b/_{60}$ respectively. After repeating this procedure several times, giving necessary corrections for the atomic coordinates, the maxima in the electron maps coincided with the atomic coordinates chosen. In Fig. 4 and in Table 3 respectively are shown the electron density projected only on (010) plane and atomic coordinates, both finally obtained.

Table 3

Atom	Number of atoms in a unit cell	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$
Si_{I}	2	0.329	0.750	0.058
Si_{II}	2	0.690	0.250	0.279
Si_{III}	2	0.189	0.750	0.317
Al_{I}	2	0.000	0.000	0.000
Al_{II}	2	0.000	0.000	0.500
(Fe^{III}, Fe^{II})	2	0.297	0.250	0.228
$(Ca, Ce)_{I}$	2	0.755	0.750	0.150
$(Ca, Ce)_{II}$	2	0.603	0.750	0.421
O_{I}	4	0.222	0.000	0.064
O_{II}	4	0.307	0.950	0.356
O_{III}	4	0.803	0.000	0.350
O_{IV}	2	0.038	0.250	0.139
O_{V}	2	0.038	0.750	0.139
O_{VI}	2	0.083	0.750	0.408
O_{VII}	2	0.517	0.750	0.175
O_{VIII}	2	0.528	0.250	0.317
O_{IX}	2	0.625	0.250	0.083
OH	2	0.083	0.250	0.408

In Tables 4, 5 an 6 are summarized the observed and calculated structure factors for *h0l*, *0kl* and *hk0* reflexions respectively. The calculated values are those which were calculated with atomic coordinates finally obtained and the observed values are those which were, at the final stage of the analysis, rendered comparable on an approximately absolute scale for the benefit of comparison with the calculated ones, by multiplying the factors of $\frac{k}{\exp\left(-B\frac{\sin^2\theta}{\lambda^2}\right)}$ respectively.

Table 4

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
100	5° 26′	10.422	0.06	—	-16
200	10° 56′	4.998	0.12	29	-86
300	16° 30′	3.127	0.18	80	98
400	22° 16′	2.150	0.25	68	73
500	28° 15′	1.564	0.31	32	39
600	34° 37′	1.204	0.37	—	-11
700	41° 34′	1.022	0.43	—	7
800	49° 12′	1.032	0.49	16	17
900	58° 23′	1.347	0.55	—	-5
10,00	71° 06′	2.650	0.61	49	44

Table 4 (cont.)

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
001	4° 46′	11.912	0.05	—	-4
101	8° 38′	6.441	0.10	7	29
201	13° 43′	3.880	0.15	37	-88
301	19° 10′	2.605	0.21	5	9
401	24° 54′	1.855	0.27	—	-6
501	31° 00′	1.382	0.33	2	-1
601	37° 29′	1.105	0.39	51	36
701	44° 33′	1.000	0.46	85	-76
801	52° 42′	1.110	0.52	—	1
901	62° 53′	1.653	0.58	56	77
002	9° 36′	5.752	0.11	12	-13
102	12° 55′	4.154	0.15	34	48
202	17° 29′	2.917	0.19	110	134
302	22° 40′	2.101	0.25	12	-28
402	28° 17′	1.563	0.31	21	-18
502	34° 18′	1.217	0.37	100	108
602	40° 57′	1.030	0.43	24	-35
702	48° 26′	1.022	0.49	20	-18
802	57° 15′	1.368	0.55	15	33
902	69° 04′	2.329	0.61	41	43
003	14° 27′	3.514	0.16	7	-5
103	17° 35′	2.895	0.20	12	20
203	21° 50′	2.206	0.24	56	-76
303	26° 47′	1.681	0.29	29	-6
403	32° 17′	1.286	0.35	66	-82
503	38° 30′	1.078	0.40	46	9
603	45° 15′	1.000	0.46	56	67
703	53° 08′	1.123	0.52	66	-52
803	63° 04′	1.669	0.58	19	15
004	19° 26′	2.600	0.22	27	-43
104	22° 30′	2.121	0.25	58	-48
204	26° 34′	1.700	0.29	58	74
304	31° 28′	1.355	0.34	27	57
404	36° 52′	1.123	0.39	88	61
504	43° 07′	1.007	0.44	5	-23
604	50° 19′	1.052	0.50	7	35
704	59° 02′	1.384	0.56	107	94
005	24° 36′	1.885	0.27	27	26
105	27° 39′	1.611	0.30	61	-82
205	31° 36′	1.348	0.34	10	-4
305	36° 35′	1.132	0.39	129	106
405	42° 09′	1.015	0.44	12	-17
505	48° 36′	1.024	0.49	49	-45

Table 4 (cont.)

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
605	56° 28′	1.251	0.54	15	−27
006	29° 57′	1.446	0.32	7	12
106	33° 04′	1.272	0 35	—	1
206	37° 10′	1.124	0.39	54	54
306	42° 09′	1.015	0.44	—	1
406	47° 57′	1.017	0.48	95	62
506	55° 05′	1.192	0.53	15	15
606	64° 10′	1.765	0.58	85	44
007	35° 40′	1.164	0.39	63	55
107	38° 56′	1.068	0.41	46	−9
207	43° 07′	1.007	0.44	73	38
307	48° 20′	1.020	0.49	56	−21
407	54° 47′	1.180	0.53	—	1
507	63° 04′	1.669	0.58	80	55
607	75° 49′	3.734	0.63	63	−79
008	41° 41′	1.020	0.43	12	−11
108	45° 15′	1.000	0.46	146	112
208	49° 50′	1.043	0.50	51	−46
308	55° 42′	1.217	0.54	15	5
408	63° 15′	1.684	0.58	66	59
009	48° 22′	1.021	0.49	7	−4
109	52° 22′	1.101	0.51	19	2
209	57° 44′	1.312	0.55	110	60
309	64° 54′	1.835	0.59	80	−55
00,10	56° 09′	1.236	0.54	34	−33
10,10	60° 59′	1.509	0 57	—	4
00,11	66° 04′	1.955	0.59	73	−82
10,11	73° 21′	3.094	0.62	49	−33
$10\bar{1}$	5° 31′	10.258	0.06	—	15
$20\bar{1}$	9° 53′	5.576	0.11	—	−17
$30\bar{1}$	15° 05′	3.478	0.17	—	15
$40\bar{1}$	20° 39′	2.370	0.23	154	161
$50\bar{1}$	26° 25′	1.713	0.29	44	−50
$60\bar{1}$	32° 35′	1.296	0.35	20	−24
$70\bar{1}$	39° 14′	1.061	0.41	22	36
$80\bar{1}$	46° 31′	1.004	0.47	37	56
$90\bar{1}$	55° 05′	1.192	0.53	12	−4
$10,0\bar{1}$	66° 04′	1.955	0.59	85	−88
$10\bar{2}$	8° 49′	6.300	0.10	10	31
$20\bar{2}$	11° 05′	4.924	0.12	12	51
$30\bar{2}$	15° 10′	3.455	0.17	78	112
$40\bar{2}$	20° 05′	2.456	0.22	58	−61
$50\bar{2}$	25° 31′	1.796	0.28	80	65

Table 4 (cont.)

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
$60\bar{2}$	31° 18′	1.365	0.34	17	37
$70\bar{2}$	37° 46′	1.097	0.40	44	14
$80\bar{2}$	44° 41′	1.000	0.46	122	96
$90\bar{2}$	52° 42′	1.110	0.52	34	−6
$10,0\bar{2}$	62° 45′	1.643	0.58	15	16
$10\bar{3}$	13° 05′	4.094	0.15	—	−38
$20\bar{3}$	13° 58′	3.801	0.16	10	50
$30\bar{3}$	16° 46′	3.068	0.19	39	−35
$40\bar{3}$	20° 49′	2.346	0.23	32	18
$50\bar{3}$	25° 37′	1.785	0.28	10	17
$60\bar{3}$	31° 00′	1.382	0.33	27	50
$70\bar{3}$	37° 01′	1.119	0.39	32	50
$80\bar{3}$	43° 36′	1.004	0.45	166	−123
$90\bar{3}$	51° 13′	1.072	0.51	34	35
$10,0\bar{3}$	60° 31′	1.477	0.57	51	57
$10\bar{4}$	17° 47′	2.857	0.20	34	78
$20\bar{4}$	17° 48′	2.854	0.20	17	−24
$30\bar{4}$	19° 32′	2.543	0.22	29	34
$40\bar{4}$	22° 38′	2.105	0.25	46	−45
$50\bar{4}$	26° 43′	1.687	0.29	20	−23
$60\bar{4}$	31° 38′	1.346	0.34	144	141
$70\bar{4}$	37° 10′	1.114	0.39	—	7
$80\bar{4}$	42° 16′	1.014	0.44	37	−5
$90\bar{4}$	50° 33′	1.057	0.50	102	62
$10,0\bar{4}$	59° 19′	1.401	0.56	41	54
$11,0\bar{4}$	71° 32′	2.727	0.62	5	6
$10\bar{5}$	22° 41′	2.099	0.25	17	44
$20\bar{5}$	22° 11′	2.161	0.24	34	50
$30\bar{5}$	23° 07′	2.047	0.25	37	−77
$40\bar{5}$	25° 23′	1.808	0.28	15	−32
$50\bar{5}$	28° 45′	1.528	0.31	24	39
$60\bar{5}$	33° 04′	1.272	0.35	76	−60
$70\bar{5}$	38° 04′	1.089	0.40	12	−6
$80\bar{5}$	43° 50′	1.003	0.45	73	−47
$90\bar{5}$	50° 40′	1.059	0.50	7	18
$10,0\bar{5}$	59° 02′	1.384	0.56	51	49
$11,0\bar{5}$	70° 39′	2.574	0.61	85	−60
$10\bar{6}$	27° 52′	1.594	0.30	183	165
$20\bar{6}$	26° 57′	1.667	0.29	95	−69
$30\bar{6}$	27° 19′	1.637	0.30	97	−99
$40\bar{6}$	28° 53′	1.519	0.31	161	165
$50\bar{6}$	31° 38′	1.346	0.34	27	49
$60\bar{6}$	35° 12′	1.181	0.37	41	17

Tab'e 4 (cont.)

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
$70\bar{6}$	39° 50′	1.049	0.42	5	-23
$80\bar{6}$	44° 57′	1.000	0.46	37	24
$90\bar{6}$	51° 35′	1.080	0.51	71	54
$10,0\bar{6}$	59° 39′	1.421	0.56	15	-19
$11,0\bar{6}$	70° 50′	2.604	0.61	22	31
$10\bar{7}$	33° 23′	1.258	0.36	10	14
$20\bar{7}$	32° 06′	1.321	0.34	5	6
$30\bar{7}$	31° 56′	1.330	0.34	—	3
$40\bar{7}$	33° 04′	1.272	0.35	19	-19
$50\bar{7}$	35° 04′	1.186	0.37	10	12
$60\bar{7}$	38° 12′	1.086	0.40	44	-45
$70\bar{7}$	42° 16′	1.014	0.44	—	-17
$80\bar{7}$	47° 14′	1.009	0.48	29	46
$90\bar{7}$	53° 25′	1.132	0.52	34	-33
$10,0\bar{7}$	61° 10′	1.522	0.57	12	-9
$11,0\bar{7}$	72° 34′	2.928	0.62	37	-40
$10\bar{8}$	39° 14′	1.061	0.41	12	-13
$20\bar{8}$	37° 38′	1.101	0.40	78	69
$30\bar{8}$	37° 10′	1.114	0.39	110	103
$40\bar{8}$	37° 46′	1.094	0.40	44	49
$50\bar{8}$	39° 23′	1.058	0.41	34	-45
$60\bar{8}$	41° 59′	1.017	0.43	95	65
$70\bar{8}$	45° 26′	1.000	0.46	93	86
$80\bar{8}$	50° 08′	1.049	0.50	30	-33
$90\bar{8}$	56° 06′	1.234	0.54	58	39
$10,0\bar{8}$	63° 46′	1.729	0.58	7	-10
$11,0\bar{8}$	75° 49′	3.734	0.63	12	-7
$10\bar{9}$	45° 29′	1.000	0.46	—	-15
$20\bar{9}$	43° 35′	1.004	0.45	49	-50
$30\bar{9}$	42° 51′	1.008	0.44	49	58
$40\bar{9}$	43° 00′	1.007	0.44	24	-17
$50\bar{9}$	44° 04′	1.002	0.45	19	-6
$60\bar{9}$	46° 16′	1.003	0.47	7	13
$70\bar{9}$	49° 31′	1.037	0.49	40	34
$80\bar{9}$	53° 54′	1.149	0.52	12	16
$90\bar{9}$	59° 39′	1.421	0.56	66	-62
$10,0\bar{9}$	67° 36′	2.134	0.60	71	56
$10,\bar{10}$	52° 42′	1.110	0.52	51	31
$20,\bar{10}$	50° 22′	1.053	0.50	139	111
$30,\bar{10}$	49° 04′	1.030	0.49	19	-41
$40,\bar{10}$	48° 51′	1.027	0.49	71	23
$50,\bar{10}$	49° 41′	1.040	0.50	33	36
$60,\bar{10}$	51° 32′	1.079	0.51	—	-2

Table 4 (cont.)

h0l	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
70,$\bar{10}$	54° 29′	1.169	0.53	124	88
80,$\bar{10}$	58° 42′	1.365	0.55	12	−6
90,$\bar{10}$	64° 42′	1.815	0.59	29	−31
10,0,$\bar{10}$	65° 22′	1.881	0.59	29	53
10,$\bar{11}$	61° 21′	1.535	0.57	49	34
20,$\bar{11}$	58° 23′	1.347	0.55	27	18
30,11	56° 28′	1.251	0.54	15	−15
40,$\bar{11}$	55° 51′	1.223	0.54	44	−51
50,$\bar{11}$	56° 18′	1.243	0.54	15	0
60,$\bar{11}$	57° 53′	1.320	0.55	56	67
70,$\bar{11}$	60° 49′	1.498	0.57	37	−39
80,$\bar{11}$	65° 06′	1.855	0.59	19	12
20,$\bar{12}$	68° 50′	2.296	0.61	73	44
30,$\bar{12}$	66° 04′	1.955	0.59	37	−13
40,$\bar{12}$	64° 42′	1.815	0.59	20	−21
50,$\bar{12}$	64° 42′	1.815	0.59	122	87
60,$\bar{12}$	68° 13′	2.213	0.60	19	−24

Table 5

0kl	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
001	4° 47′	11.868	0.05	—	−4
002	9° 35′	5.764	0.11	12	−13
003	14° 27′	3.655	0.16	7	−5
004	19° 27′	2.677	0.22	27	−43
005	24° 35′	1.887	0.27	27	26
006	29° 57′	1.446	0.32	7	12
007	35° 40′	1.164	0.38	63	55
008	41° 41′	1.020	0.43	12	−11
009	48° 22′	1.021	0.49	7	−4
00,10	56° 09′	1.236	0.54	34	−33
00,11	66° 04′	1.955	0.59	73	−82
010	7° 42′	7.265	0.09	—	0
011	9° 05′	6.105	0.10	29	34
012	12° 20′	4.376	0.14	15	42
013	16° 28′	3.135	0.18	85	127
014	21° 02′	2.315	0.23	32	−23
015	25° 55′	1.758	0.28	37	−48
016	31° 08′	1.375	0.34	39	12
017	36° 44′	1.128	0.39	44	55
018	42° 51′	1.008	0.44	97	106

Table 5 (cont.)

Okl	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
019	49° 25′	1.036	0.49	37	-24
01,10	57° 15′	1.288	0.55	44	39
01,11	67° 27′	2.115	0.60	51	-52
020	15° 33′	3.356	0.17	180	-260
021	16° 18′	3.173	0.18	39	-37
022	18° 24′	2.740	0.20	58	84
023	21° 29′	2.253	0.24	71	102
024	25° 18′	1.815	0.28	41	55
025	29° 40′	1.465	0.32	24	-34
026	34° 37′	1.204	0.37	71	77
027	39° 59′	1.046	0.42	105	-96
028	45° 46′	1·001	0.47	56	44
029	52° 31′	1.105	0.52	—	8
02,10	60° 49′	1.498	0.57	19	29
02,11	72° 17′	2.870	0.62	44	71
030	23° 43′	1.979	0.26	—	0
031	24° 15′	1.870	0.27	19	-24
032	25° 48′	1.768	0.28	10	26
033	28° 15′	1.564	0.31	54	-100
034	31° 28′	1.356	0.34	37	76
035	35° 23′	1.174	0.38	32	39
036	39° 50′	1.049	0.42	39	58
037	44° 57′	1.000	0.46	29	-48
038	50° 56′	1.065	0.50	51	-54
039	58° 03′	1.329	0.55	12	26
03,10	67° 27′	2.115	0.60	—	-2
040	32° 25′	1.305	0.35	224	271
041	32° 53′	1.281	0.35	10	-1
042	34° 08′	1.224	0.36	10	-5
043	36° 16′	1.143	0.38	7	-12
044	39° 05′	1.065	0.41	—	-4
045	42° 41′	1.010	0.44	19	25
046	47° 01′	1.007	0.48	—	5
047	52° 14′	1.097	0.51	34	45
048	58° 33′	1.356	0.55	—	-10
049	66° 47′	2.036	0.60	—	-2
050	42° 09′	1.015	0.44	—	0
051	42° 34′	1.011	0.44	24	22
052	43° 36′	1.004	0.45	24	24
053	45° 34′	1.001	0.46	73	88
054	48° 23′	1.021	0.49	—	-1
055	51° 57′	1.090	0.51	37	-37
056	56° 37′	1.258	0.54	—	-1

Table 5 (cont.)

0kl	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
057	62° 34′	1.628	0.58	37	41
058	70° 39′	2.574	0.61	58	83
060	53° 25′	1 132	0.52	100	-111
061	53° 54′	1.149	0.52	—	0
062	55° 06′	1.193	0.53	29	48
063	57° 15′	1.288	0.55	29	47
064	60° 21′	1.466	0.56	27	36
065	64° 42′	1.815	0.59	12	-24
066	71° 06′	2.650	0.61	41	49
070	69° 29′	2.390	0.61	—	0
071	70° 09′	2.492	0.61	15	-16
072	72° 05′	2.831	0.62	—	14
073	75° 49′	3.734	0.63	44	-64

Table 6

hk0	θ	$\frac{1+\cos^2 2\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
100	5° 26′	10.423	0.06	—	-16
200	10° 55′	5.006	0.12	29	-86
300	16° 31′	3.124	0.18	80	98
400	22° 16′	2.150	0.25	68	73
500	28° 17′	1.560	0.31	32	39
600	34° 37′	1.204	0.37	—	-11
700	41° 34′	1.022	0.43	—	7
800	49° 12′	1.032	0.49	—	17
900	58° 23′	1.347	0.55	—	-5
10,00	71° 06′	2.650	0.61	49	44
010	7° 42′	7.265	0.09	—	0
110	9° 27′	5.851	0.11	8	-72
210	13° 25′	3.979	0.15	10	43
310	18° 19′	2.755	0.20	20	23
410	23° 42′	1.981	0.26	8	7
510	29° 30′	1.476	0.32	60	-77
610	35° 40′	1.164	0.38	—	-4
710	42° 34′	1.011	0.44	113	90
810	50° 11′	1.050	0.50	53	-50
910	59° 29′	1.411	0.56	—	-8
10,10	72° 45′	2.965	0.62	—	0
020	15° 33′	3.356	0.17	180	-260
120	16° 31′	3.124	0.18	95	90
220	19° 10′	2.604	0.21	25	32
320	23° 00′	2.061	0.25	20	-31

Table 6 (cont.)

hk0	θ	$\frac{1+\cos^2 1\theta}{\sin 2\theta}$	$\frac{\sin\theta}{\lambda}$	*Fo*	*Fc*
420	27° 40′	1.609	0.30	48	48
520	33° 04′	1.272	0.35	25	32
620	38° 56′	1.068	0.41	58	54
720	45° 36′	1.001	0.46	15	28
820	53° 25′	1.132	0.52	35	13
920	63° 16′	1.686	0.58	68	57
10,20	79° 35′	5.267	0.64	—	7
030	23° 43′	1.979	0.26	—	0
130	24° 24′	1.906	0.27	75	69
230	26° 24′	1.714	0.29	58	-38
330	29° 30′	1.476	0.32	15	-27
430	33° 32′	1.251	0.36	10	-9
530	38° 30′	1.078	0.40	58	70
630	44° 04′	1.002	0.45	—	-2
730	50° 46′	1.061	0.50	105	-82
830	59° 02′	1.384	0.56	53	47
930	70° 24′	2.532	0.61	—	3
040	32° 25′	1.305	0.35	224	271
140	33° 04′	1.272	0.35	10	-10
240	34° 37′	1.204	0.37	43	-55
340	37° 18′	1.110	0.39	68	70
440	41° 07′	1.028	0.43	30	46
540	45° 36′	1.001	0.46	38	33
640	51° 21′	1.075	0.51	—	-10
740	58° 23′	1.347	0.55	—	-3
840	68° 03′	2.191	0.60	13	17
050	42° 09′	1.015	0.44	—	0
150	42° 34′	1.011	0.44	25	-33
250	44° 04′	1.002	0.45	38	28
350	46° 39′	1.005	0.47	20	8
450	50° 19′	1.052	0.50	20	12
550	55° 05′	1.192	0.53	50	-54
650	61° 21′	1.535	0.57	—	-2
750	70° 24′	2.532	0.61	75	75
060	53° 25′	1.132	0.52	100	-111
160	54° 03′	1.154	0.53	98	64
260	55° 32′	1.210	0.54	65	46
360	58° 23′	1.347	0.55	—	-8
460	62° 34′	1.628	0.58	45	25
560	68° 50′	2.296	0.61	10	17
070	69° 29′	2 390	0.61	—	0
170	70° 24′	2.516	0.61	30	50

The proportional constant, k, and the temperature factor, B, were found graphically, plotting the values of $\log Fo/Fc$ against those of $\sin^2\theta/\lambda^2$. The accuracy of the structure estimated from the value of

$$\frac{\Sigma \big| |Fo| - |Fc| \big|}{\Sigma |Fo|}$$

is 0.311, 0.316 and 0.289 for $h0l$, $0kl$ and $hk0$ reflexions respectively.

Description of the structure

In Fig. 5 is illustrated the structure of allanite the same as that of epidote, hence no detailed description about it.

The structure is of the mixed silicate type, containing both the single and double tetrahedral groups, SiO_4 and Si_2O_7. These separate groups are joined to one another by Al, (Fe^{III}, Fe^{II}) and (Ca, Ce) atoms on the one hand and by O atoms and OH groups on the other. The framework of the structure is composed of AlO_4 and AlO_3 (OH) chains which are stretched indefinitely along the b– axis. The chains are formed of octahedral groups of six O atoms and of five O atoms and one OH group around Al atom, and each group shares an edge with a neighbour on either side. (Fe^{III}, Fe^{II}) atoms too have an octahedral coordination. (Ca, Ce) atoms are eightfold coordinated by O atoms in a rather irregular fashion.

Taking these structural aspects into account the formula of allanite can be described, after that of epidote given by Ito,[10] as follows:

$$OH\ (Ca,\ Ce)_2\ (Fe^{III},\ Fe^{II})\ Al_2O\ Si_2O_7\ SiO_4$$

Relationship between allanite and epidote

From the present analysis it is found that allanite and epidote have almost the same cell-dimensions and the same atom-coordinates. On the other hand, no continuous series is known as yet between epidote and allanite. These two minerals may, therefore, be said to be in a relationship of *isotypie*. Taking the chemical constitution of allanite into consideration, however, the term *isotypie* is inapplicable to the present case. It would better be said that allanite is nothing else than epidote in which a part of Ca atoms have been replaced by rare earth atoms, and in which because of the neutralization also Fe^{III} atoms have been replaced by Fe^{II} atoms just as many as Ca atoms by Ce atoms.

Summarizing the results of the chemical analyses hitherto carried out by many authors, the content of CaO in allanite amounts to about 8~18%. (There are some data in which the content of CaO amounts only to about 3%. These specimens have, however, probably suffered weathering.) The content of CaO in epidote commonly amounts to about 23%. Accordingly, in the structure of

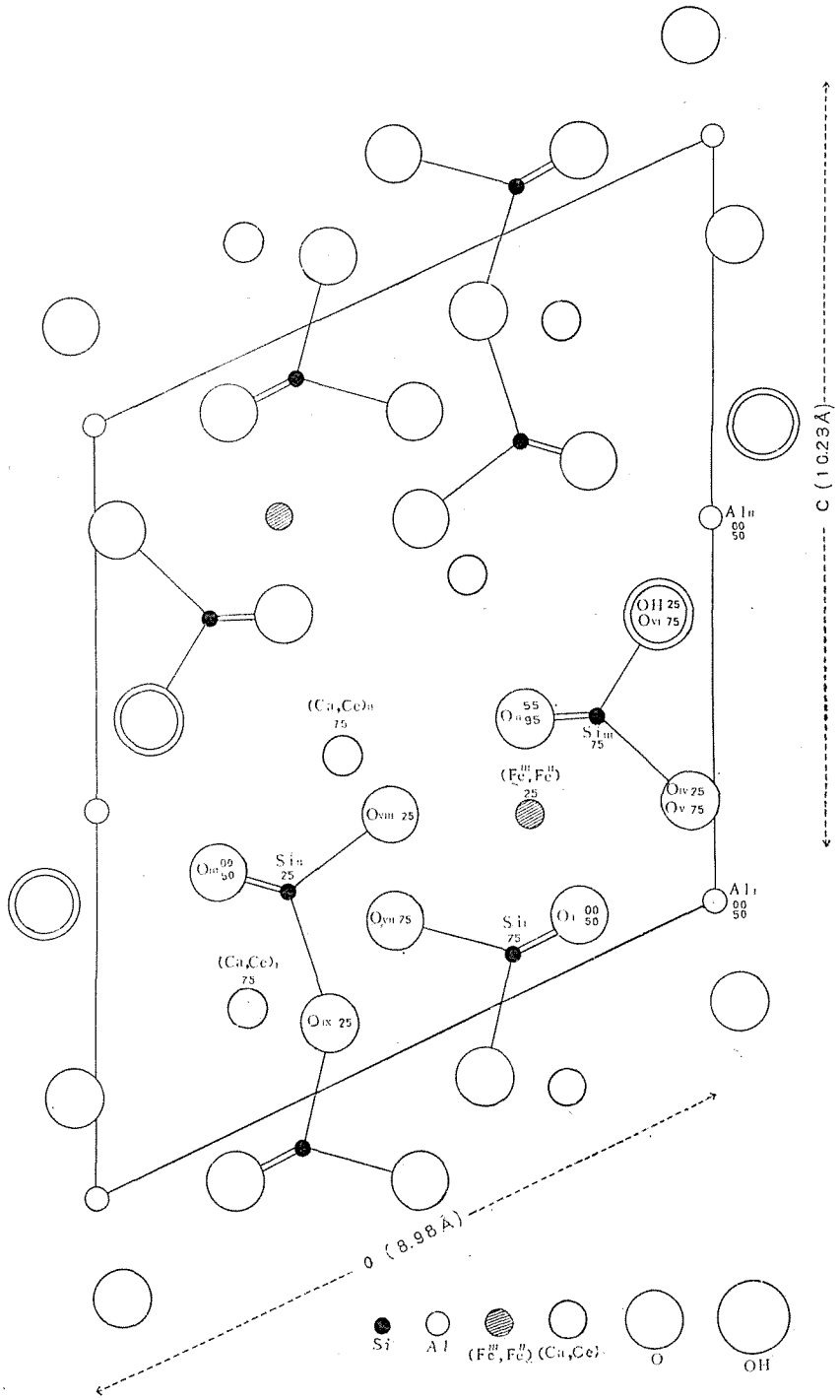

Fig. 5. The structure of allanite projected on (010) plane.

epidote about 22~65% of *Ca* atoms are likely to be replaceable by rare earth atoms.

Acknowledgment

The writer wishes to express his sincere thanks to Dr. T. ITO, Professor of Tokyo University and Kyoto University, who gave him valuable suggestions throughout this work. The writer is also indebted to Dr. M. KAWANE, Professor of Kyoto University, for his kindness in granting him the use of the X-ray apparatus.

References

1) ITO, T., MORIMOTO, N. and SADANAGA, R.: On the structure of epidote; *Acta Cryst.* **7**, 53 (1954).
2) DANA, E. S.: A Textbook of Mineralogy, 4th edition (1932).
3) CORRENS, C. W.: Einführung in die Minerologie (1949).
4) KRAUS, E. H., HUNT, W. F. and RAMSDELL, L. S.: Mineralogy, 4th edition (1951).
5) WINCHELL, A. N.: Elements of Optical Mineralogy, 4th edition (1951).
6) HILLER, J. E.: Grundriss der Kristallchemie (1952).
7) MACHATSCHKI, F.: Spezielle Mineralogie auf Geochemischer Grundlage (1953).
8) *Loc. cit.*
9) *Loc. cit.*
10) *Loc. cit.*