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The determination and refinement of the crystal structure of yugawaralite

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Auszug

Die Struktur von Yugawaralit, $CaAl_2Si_6O_{16} \cdot 4H_2O$, wurde neu bestimmt und nach der Methode der kleinsten Quadrate bis zu $R = 0{,}14$ (gewichtet: $R = 0{,}13$) verfeinert. Die Gitterkonstanten sind $a = 6{,}73$ Å, $b = 13{,}96$ Å, $c = 10{,}02$ Å, $\beta = 111° 30'$; Raumgruppe Pc; $Z = 2$. Die Struktur wird charakterisiert durch viergliedrige Ringe nahezu senkrecht zur c-Achse, fünfgliedrige Ringe beiderseits der ac-Ebene und unter etwa 65° zu dieser und achtgliedrige Ringe, die Kanäle parallel der a- und der c-Achse einschließen. Die Kanäle verlaufen in Ebenen durch $\frac{1}{4}b$ und $\frac{3}{4}b$; ihr Durchmesser ist 3,7 Å.

Aluminium vertritt Silicium in vier der acht unabhängigen Si-Tetraeder. Die mittleren Abstände sind 1,61 Å für Si—O und 1,69 Å für (Al,Si)—O. Die beiden Ca-Atome sind auf zwei zweizählige Punktlagen verteilt; sie befinden sich in der Nähe der Punkte, in denen sich die Achsen der Kanäle schneiden. Sie sind von je vier O-Atomen des Gerüsts, das eine Ca-Atom außerdem von vier, das andere von drei Wassermolekülen umgeben. Es wird vermutet, daß ein weiteres Wassermolekül auch beim zweiten Ca-Atom die Achterkoordination vervollständigt. Alle Wassermoleküle sind annähernd 2,45 Å von den Ca-Atomen entfernt.

Obwohl Yugawaralit einige Merkmale mit den anderen Zeolithen gemeinsam hat, läßt sich das Mineral doch in keine der sieben Strukturgruppen der Zeolithe einreihen. Es wird daher vorgeschlagen, eine achte Gruppe anzuschließen.

Abstract

Yugawaralite is monoclinic, $a = 6.73$, $b = 13.96$, $c = 10.02$ Å, $\beta = 111°30'$, space group Pc, and $Z = 2$ for ideal composition $CaAl_2Si_6O_{16} \cdot 4H_2O$. Refinement of the structure of yugawaralite by least-squares technique yields a discrepancy index, R, of .14 and a weighted R of .13.

The structure of yugawaralite is characterized by four-membered ring groups approximately perpendicular to the c axis, by five-membered ring groups at about 65° to either side of the ac plane, and by eight-membered ring groups which form channels parallel to the a and c axes. The axes of these channels lie on planes parallel to the ac plane at distances of approximately

.25 and .75 on the b axis. Aluminum substitutes for silicon in four of the eight independent silica tetrahedra. The average bond distance for Si—O is 1.61 Å, whereas in aluminum-substituted tetrahedra the distance is increased to 1.68 Å. Yugawaralite has relatively open channels in two directions. These are equal in size with an effective diameter of approximately 3.7 Å. The small channels would limit its use as a molecular sieve or water softener. Two calcium atoms in yugawaralite occupy positions near the intersections of the axes of the eight-membered ring channels. One calcium atom is coordinated to four framework-oxygen atoms and four water molecules. The other calcium atom is coordinated to four oxygen atoms and three water molecules although it is suspected that another water molecule is present to provide an eightfold coordination. All water molecules are at approximately 2.45 Å from the calcium atoms.

Although yugawaralite has a few characteristics in common with the other zeolites, it does not have enough of these characteristics to place it in any of the seven defined structural groups. It is suggested that an eighth group be created which would include the new linkages contained in yugawaralite.

Introduction

Yugawaralite is a rare calcium zeolite. It has been reported from Kanagawa Prefecture, Japan (SAKURAI and HAYASHI, 1952), where it occurs in veinlets as an alteration product of an andesitic tuff, and from Heinabergsjökull, southern Iceland (BARRER and MARSHALL, 1965). Yugawaralite is found in an environment which is oversaturated with respect to SiO_2 (COOMBS, ELLIS, FYFE and TAYLOR, 1959). A Sr near-yugawaralite has been synthesized by BARRER and MARSHALL (1965) under hydrothermal conditions from aqueous gels at temperatures between 270° and 350°C. The mineral itself has not yet been synthesized.

The determination and refinement of the structure of yugawaralite was initiated to provide information to aid in predicting its genesis, stability, and geologic usefulness. It was hoped that the knowledge of the crystal structure would lead to prediction of its ion-exchange properties.

Previous work

SAKURAI and HAYASHI (1952) published the first data on yugawaralite. They described the external crystal morphology, as well as physical, optical, chemical, and thermal properties. Also given were unit-cell parameters of $a = 13.26$, $b = 13.63$, $c = 9.73$ Å, $\beta = 68°30'$ determined from x-ray oscillation photographs. SMITH and RINALDI (1962) mentioned gismondite and yugawaralite as possible candidates for structures composed of four- and eight-membered rings of silica

tetrahedra. New unit-cell parameters were presented by BARRER and MARSHALL (1965) from Weissenberg and precession photographs. These were as follows: $a = 6.73$, $b = 13.95$, $c = 10.03$ Å, $\beta = 111°30'$, space group Pc. Both cells are illustrated in Fig. 1. Recently, KERR and WILLIAMS (1967) have published an unrefined structure of yugawaralite.

Both the set of new parameters and the unrefined structure of yugawaralite were derived independently by us.

Experimental

Morphology, optical properties, and density

The yugawaralite specimen used in this investigation was from near the type locality, Yugawara Hot Spring, Kanagawa Prefecture, Japan. Crystals occur in veinlets in a gray tuff. Euhedral crystals of yugawaralite had prominent {010}, {110}, {011}, {111} forms with perfect to imperfect (010) cleavage.

The optical properties of the yugawaralite specimen, as determined by the immersion method on crystal fragments are as follows: $n_x = 1.496$, $n_y = 1.497$, $n_z = 1.504 \pm 0.001$; biaxial (+); $2V = 62°$; optic-axis plane (010). The optical properties are consistent with the values presented by SAKURAI and HAYASHI (1952).

The density of yugawaralite, measured with a Berman balance, was 2.202 ± 0.005 g/cm^3, the mean of three independent measurements of crystal fragments having an average weight of 12 milligrams. This density compares favorably with the values of SAKURAI and HAYASHI (1952) and with those of the other zeolites presented by DEER, HOWIE and ZUSSMAN (1963).

Table 1. *Chemical analysis of yugawaralite*

Oxide	Percent
SiO_2	60.74
Al_2O_3	18.17
Fe_2O_3	.09
CaO	10.99
MgO	.01
Na_2O	.15
K_2O	.02
H_2O (+)	9.68
H_2O (−)	2.85
Total	102.70

Chemical analysis

A chemical analysis by Booth, Garrett, and Blair, Inc., Philadelphia, Pennsylvania, of crystals from which the structure was determined is given in Table 1. The chemical formula of yugawaralite based on 32 oxygen atoms in the anhydrous cell is

$$Ca_{2.24}(Na_2, K_2, Mg)_{0.62}Al_{4.22}Si_{11.56}O_{32} \cdot 7.95\,H_2O.$$

The unit cell contains two formula weights of the ideal formula $CaAl_2Si_6O_{16} \cdot 4\,H_2O$.

Powder-diffraction data

An x-ray powder-diffraction photograph was made from the yugawaralite sample using Fe-filtered Co radiation. Table 2 shows the diffraction data of yugawaralite indexed on the basis of its true monoclinic cell, using $a = 6.73$ Å.

Table 2. *X-ray powder data for yugawaralite*

d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}	hkl
13.9 Å	13.95 Å	20	010					2.504 Å	2.507 Å	10	$\bar{2}21$	1.9460 Å	1.9472 Å	10	071
7.80	7.76	40	011	3.05 Å	3.05 Å	100	210				$\bar{1}04$				114
7.00	6.97	80	020				$\bar{2}10$	2.465	2.468	10	$\bar{1}14$	1.9230	1.9231	10	$\bar{1}25$
6.30	6.26	10	100				140	2.413	2.414	10	113	1.8880	1.8895	30	124
5.85	5.81	90	$\bar{1}11$	2.917	2.920	40	$\bar{1}40$	2.354	2.358	30	$\bar{1}24$				$\bar{2}42$
4.68	4.67	100	002	2.872	2.881	40	122				$\bar{2}42$	1.8705	1.8710	10	$\bar{3}41$
			120				222				004				213
			$\bar{1}20$				220	2.330	2.333	30	240	1.7840	1.7836	10	$\bar{2}54$
4.40	4.41	20	$\bar{1}12$	2.832	2.841	10	$\bar{2}20$				$\bar{2}40$				$\bar{2}63$
4.26	4.27	40	111	2.741	2.756	20	023	2.2002	2.2036	10	$\bar{2}24$	1.7468	1.7469	10	233
3.88	3.88	30	022	2.705	2.719	40	141	2.1350	2.1362	20	222				080
			$\bar{1}22$				$\bar{2}13$				$\bar{1}53$	1.7148	1.7150	20	$\bar{2}71$
			$\bar{1}03$	2.672	2.674	20	$\bar{1}33$	2.0875	2.0872	40	300				081
3.75	3.76	30	130	2.631	2.636	20	051				143	1.6850	1.6852	10	163
			$\bar{1}30$				211	2.0020	2.0040	20	$\bar{3}31$				$\bar{1}81$
3.23	3.23	80	131	2.570	2.576	10	$\bar{2}32$				320	1.6440	1.6439	10	$\bar{2}16$
							$\bar{2}23$				$\bar{3}20$	1.6094	1.6093	10	204

Differential thermal analysis

Two differential thermal-analysis curves (Fig. 2) were run using a Stone Model KA-DTA series unit. One curve, using a 200-mg sample and a tubular sample holder, is similar to the one reported by SAKURAI and HAYASHI (1952). The other curve, using a 0.1-mg sample and a micro-micro sample holder, is similar to the first curve but differs in the temperatures at which the endothermic peaks occur. The lower temperatures of the endotherms from the small sample are expected.

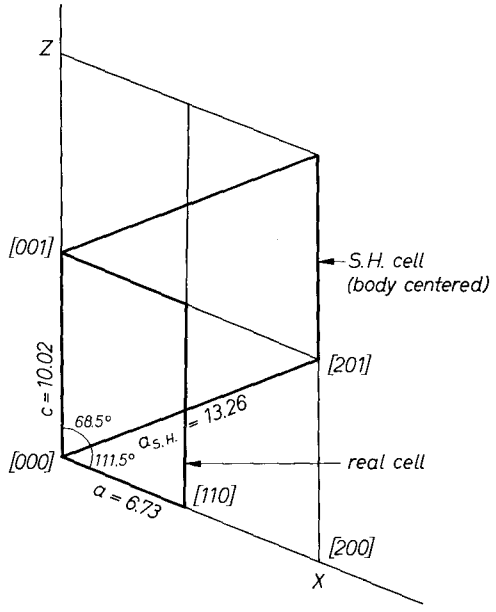

Fig. 1. Relationsship between the cell determined by SAKURAI and HAYASHI (S.H.) and the real cell

A sample was placed in a Stone furnace attached to the x-ray generator. Diffraction patterns were taken as the sample was heated at various temperatures selected from the differential thermal-analysis curve. An endothermic peak occurs at 80 °C representing the loss of absorbed and adsorbed water. A second endothermic peak occurs at 240 °C representing the loss of structural water bonded to the

Table 3. *X-ray diffraction data for yugawaralite heated to, and kept at, a temperature of* 420 °C

Peak	*d*	*I*	Peak	*d*	*I*
1	6.46	30	10	3.75	40
2	5.40	10	11	3.51	20
3	4.51	90	12	3.23	50
4	4.48	90	13	3.02	50
5	4.44	100	14	2.91	30
6	4.35	70	15	2.84	40
7	4.20	20	16	2.74	30
8	4.06	80	17	2.53	20
9	3.88	20	18	1.88	20

calcium ions in the channels. A pair of endothermic peaks occur at about 400 °C marking the formation of new unidentified mineral phases as shown by a diffraction pattern made at 420 °C (Table 3). Diffraction peaks of this new material diminish in intensity above 420 °C. A small endothermic peak at 650 °C represents the breakdown of crystalline material into a glass. A diffraction pattern run at 700 °C shows only a broad glass band centered around 3.8 Å.

Unit-cell dimensions and volume

Cell dimensions obtained from rotation, Weissenberg, and precession photographs are monoclinic, $a = 6.73$, $b = 13.96$, $c = 10.02$ Å, and $\beta = 111°30'$. The calculated unit-cell volume is 876.13 Å^3. The a parameter differs from that of SAKURAI and HAYASHI (1952).

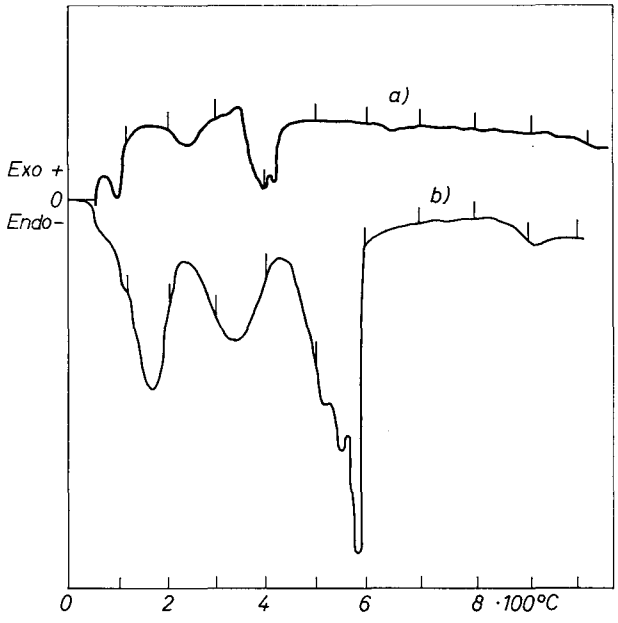

Fig. 2. Differential-thermal-analysis curves for yugawaralite; (*a*) 0.1 mg sample, micro-micro sample holder; (*b*) 200 mg sample, tubular sample holder. Heating rate: 12.5 °C/min

Collection of intensity data

Two methods were employed to obtain intensity data required to determine and refine the crystal structure. Intensities were measured from photographs made with a Weissenberg camera with equi-inclina-

tion geometry using Ni-filtered Cu radiation. The photographs were developed and measured with a modified version of the photoreversal technique proposed by MACINTYRE and THOMPSON (1960). Data were collected from two single crystals. One, mounted on the b axis, had approximate dimensions of .30 × .35 × .30 mm. The other, mounted on the c axis, had approximate dimensions of .10 × .62 × .63 mm. Nine levels of reflections from the monoclinic b axis mounting and seven levels from the monoclinic c axis were measured. Data obtained by this technique were used to determine an incomplete and unrefined structure for yugawaralite.

To improve accuracy, the intensities for the completion and refinement of yugawaralite were measured again using an automated Buerger-Supper single-crystal x-ray diffractometer controlled by an IBM 1710 unit and the procedures described by SLAUGHTER (1969). An attenuator was used and losses were negligible. The takeoff angle was 3.5°. The same yugawaralite crystal, mounted for rotation about the b axis and used in the preliminary work, was used. In all, 1450 independent reflections were measured from 17 levels ($h0l$ through h, 16, l) using Ni-filtered Cu radiation. The measured reflections comprise approximately 72 percent of the total number of reflections in the Cu$K\alpha$ limiting sphere.

All intensities were corrected for Lorentz-polarization and absorption effects using IBM 1620 computer programs written by KANE (1966).

Determination of the crystal structure

Determination of the space group

Single-crystal Weissenberg and precession photographs of yugawaralite show monoclinic symmetry with extinctions of the type $l \neq 2n$ for the reflections ($h0l$), indicating the space group Pc or $P2/c$. The zero-moment centricity test (HOWELLS, PHILLIPS and ROGERS, 1950) shown in Fig. 3 with ($h0l$), ($0kl$) and ($hk0$) reflections, suggests the mineral is noncentric and thus in space group Pc.

Determination of the trial structure

SMITH and RINALDI (1962) suggested a structure for yugawaralite composed of four- and eight-membered rings. At that time, however, the a parameter was reported as 13.26 Å. With the determination of the new a parameter these suggested possibilities were eliminated. Their spacings of 6.9 Å for one four-membered ring and 13.8 Å for

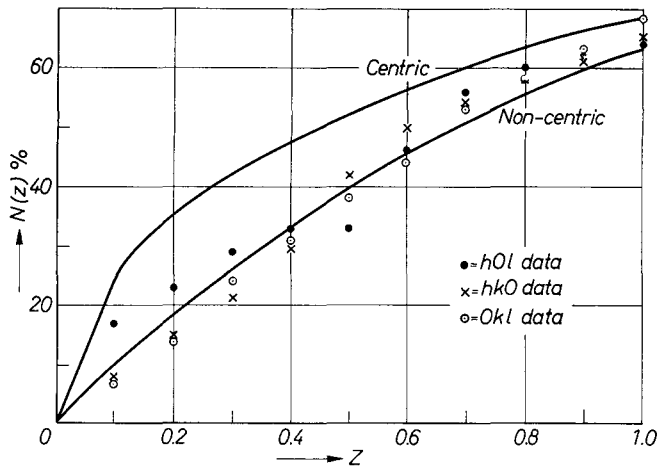

Fig. 3. Zero-moment centricity test for yugawaralite

a pair of four-membered rings placed adjacent to each other were still close to the a and b parameters of yugawaralite. Their linkings C, J and L could be possible structures.

A set of three-dimensional Patterson maps was made and examined, keeping in mind the three possible linkings. An IBM 1620 program for solution of the Patterson function by superposition methods (COREFIELD, 1965) using the minimum function retrieved five of the eight independent silicon positions from the .00, .18, .20, .26, and .50 Patterson levels along the c axis. Placement of bridging oxygen atoms approximately halfway between the silicon atoms gave initial atomic coordinates as follows:

Atom	x	y	z
Si(1)	.00	.00	.00
Si(2)	.72	.00	.18
Si(3)	.36	.13	.20
Si(4)	.36	.36	.26
Si(5)	.32	.13	.50
O(1)	.86	.00	.10
O(2)	.64	.08	.20
O(3)	.18	.08	.12
O(4)	.36	.25	.22
O(5)	.36	.13	.35

Table 4. *Unrefined atomic coordinates, occupancies, and temperature factors*

Atom	Occupancy	x	y	z	B
Si(1)	1.0	.000	.000	.000	1.0 Å^2
Si(2)	1.0	.710	.011	.181	1.0
Si(3)	1.0	.367	.141	.196	1.0
Si(4)	1.0	.364	.366	.243	1.0
Si(5)	1.0	.972	.490	.061	1.0
Si(6)	1.0	.687	.536	.247	1.0
Si(7)	1.0	.316	.644	.023	1.0
Si(8)	1.0	.314	.879	.007	1.0
O(1)	1.0	.833	.035	.065	2.0
O(2)	1.0	.610	.108	.189	2.0
O(3)	1.0	.211	.106	.068	2.0
O(4)	1.0	.368	.262	.184	2.0
O(5)	1.0	.145	.429	.114	2.0
O(6)	1.0	.548	.426	.207	2.0
O(7)	1.0	.880	.540	.150	2.0
O(8)	1.0	.066	.600	.033	2.0
O(9)	1.0	.547	.617	.189	2.0
O(10)	1.0	.300	.780	.050	2.0
O(11)	1.0	.120	.930	.000	2.0
O(12)	1.0	.520	.920	.100	2.0
O(13)	1.0	.311	.111	.354	2.0
O(14)	1.0	.401	.389	.397	2.0
O(15)	1.0	.840	.940	.350	2.0
O(16)	1.0	.784	.548	.401	2.0
Ca(1)	.5	.664	.782	.253	2.5
Ca(2)	.5	.011	.712	.472	2.5
HOH(1)	.5	.720	.240	.000	4.0
HOH(2)	.5	.880	.260	.170	4.0
HOH(3)	.5	.240	.640	.400	4.0
HOH(4)	.5	.000	.700	.350	4.0
HOH(5)	.5	.400	.820	.350	4.0
HOH(6)	.5	.960	.760	.200	4.0
HOH(7)	.5	.800	.760	.050	4.0

The remainder of the framework atoms, calcium ions, and water molecules were located by successive Fourier synthesis (Table 4). Introduction of all framework atoms reduced the discrepancy index

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

Table 5. *Final atomic parameters and standard deviations, temperature factors from both differential synthesis and least-squares refinement*

Atom	Occupancy*	x	y	z	B Differential synthesis	B Least squares
Si(1)	1.0	.9980	.0247	.9923	1.04 Å^2	1.16 Å^2
Si,Al(2)	.38, .62	.7156	.0082	.1855	.63	.30
Si,Al(3)	.59, .41	.3712	.1459	.1998	.91	.64
Si(4)	1.0	.3624	.3709	.2369	.99	.75
Si,Al(5)	.59, .41	.9787	.4996	.0655	1.05	1.37
Si(6)	1.0	.6842	.5360	.2455	.65	.42
Si,Al(7)	.38, .62	.3179	.6486	.0280	.92	1.14
Si(8)	1.0	.3131	.8768	.0034	1.13	1.29
σ		.004 Å	.005 Å	.005 Å		
O(1)	1.0	.8290	.0269	.0697	1.96	2.35
O(2)	1.0	.5921	.0992	.1857	2.57	2.35
O(3)	1.0	.2028	.1094	.0506	1.52	2.09
O(4)	1.0	.3695	.2666	.1896	1.46	1.19
O(5)	1.0	.1440	.4224	.1156	1.82	2.65
O(6)	1.0	.5518	.4321	.2011	1.22	.72
O(7)	1.0	.8394	.5484	.1524	4.75	4.93
O(8)	1.0	.0814	.6056	.0115	1.75	1.73
O(9)	1.0	.5387	.6230	.1847	1.52	.80
O(10)	1.0	.3033	.7684	.0518	2.03	2.51
O(11)	1.0	.1027	.9269	.0013	.96	2.17
O(12)	1.0	.5275	.9137	.1008	1.66	.93
O(13)	1.0	.3341	.1106	.3561	2.46	3.24
O(14)	1.0	.3985	.3834	.4010	1.64	1.97
O(15)	1.0	.8538	.9374	.3451	3.31	2.37
O(16)	1.0	.7781	.5432	.4142	2.14	2.06
σ		.019 Å	.022 Å	.023 Å		
Ca(1)	.62	.6642	.7874	.2564	1.32	1.42
Ca(2)	.41	.0179	.7179	.4697	1.42	1.10
σ		.008 Å	.008 Å	.009 Å		
HOH(1)	.78	.7427	.2397	.0077	3.57	4.21
HOH(2)	.68	.8854	.2649	.1678	4.00	2.85
HOH(3)	.16	.1407	.5629	.3193	4.00	9.50
HOH(4)	.61	.0226	.7126	.3503	4.10	.43
HOH(5)	1.0	.3674	.8487	.3237	4.18	7.90
HOH(6)	.37	.9762	.7656	.2053	4.10	.92
HOH(7)	.27	.7855	.7746	.0363	2.07	3.09
σ		.024 Å	.031 Å	.031 Å		

* Occupancy determined from differential synthesis.

from an initial value of .53 to .34. Positioning Ca ions reduced R to .27, and placing of the water molecules reduced R to .22. A twisted version of SMITH and RINALDI's J linking was the key to the basic framework of yugawaralite.

Refinement of the crystal structure

The structure of yugawaralite was refined by a combination of differential Fourier synthesis and least-squares techniques. Four cycles of differential-synthesis refinement using IBM 1620 programs written by SLAUGHTER (1964) with manual adjustment of temperature and site-occupancy factors reduced the discrepancy index to .16. Calculated atomic distances plus calculated and observed values of the electron densities, temperature factors, and curvatures indicated partial occupancy of aluminum in silicon positions 2, 3, 5, and 7

Table 6. *Interatomic distances*

Si(1)—O(1)	1.59 Å	Si,Al(5)—O(5)	1.50 Å
—O(3)	1.74	—O(7)	1.66
—O(11)	1.52	—O(8)	1.80
—O(15)	1.54	—O(16)	1.72
Mean	1.60	Mean	1.67
Si,Al(2)—O(1)	1.63	Si(6)—O(6)	1.68
—O(2)	1.51	—O(7)	1.63
—O(12)	1.82	—O(9)	1.54
—O(15)	1.82	—O(16)	1.59
Mean	1.70	Mean	1.61
Si,Al(3)—O(2)	1.68	Si,Al(7)—O(8)	1.65
—O(3)	1.60	—O(9)	1.76
—O(4)	1.69	—O(10)	1.71
—O(13)	1.75	—O(14)	1.62
Mean	1.68	Mean	1.69
Si(4)—O(4)	1.53	Si(8)—O(10)	1.59
—O(5)	1.69	—O(11)	1.58
—O(6)	1.67	—O(12)	1.50
—O(14)	1.58	—O(13)	1.54
Mean	1.62	Mean	1.56

Table 6. *(Continued)*

Si(1)—O(1)—O(3)	2.84 Å	Si(6)—O(6)—O(7)	2.67 Å
—O(1)—O(11)	2.58	—O(6)—O(9)	2.66
—O(1)—O(15)	2.46	—O(6)—O(16)	2.63
—O(3)—O(11)	2.64	—O(7)—O(9)	2.52
—O(3)—O(15)	2.58	—O(7)—O(16)	2.79
—O(11)—O(15)	2.60	—O(19)—O(16)	2.56
Si,Al(2)—O(1)—O(2)	2.53	Si,Al(7)—O(8)—O(9)	2.93
—O(1)—O(12)	2.67	—O(8)—O(10)	2.69
—O(1)—O(15)	2.98	—O(8)—O(14)	2.74
—O(2)—O(12)	2.71	—O(9)—O(10)	2.63
—O(2)—O(15)	2.95	—O(9)—O(14)	2.63
—O(12)—O(15)	2.64	—O(10)—O(14)	2.81
Si,Al(3)—O(2)—O(3)	2.46	Si(8)—O(10)—O(11)	2.53
—O(2)—O(4)	2.78	—O(10)—O(12)	2.45
—O(2)—O(13)	2.83	—O(10)—O(13)	2.64
—O(3)—O(4)	2.61	—O(11)—O(12)	2.67
—O(3)—O(13)	2.83	—O(11)—O(13)	2.55
—O(4)—O(13)	2.79	—O(12)—O(13)	2.44
Si(4)—O(4)—O(5)	2.59	Ca(1)—O(9)	2.46
—O(4)—O(6)	2.61	—O(10)	2.55
—O(4)—O(14)	2.63	—O(12)	2.31
—O(5)—O(6)	2.58	—O1(5)	2.44
—O(5)—O(14)	2.81	—HOH(4)	2.48
—O(6)—O(14)	2.68	—HOH(5)	2.48
		—HOH(6)	2.37
Si,Al(5)—O(5)—O(7)	2.82	—HOH(7)	2.35
—O(5)—O(8)	2.73		
—O(5)—O(16)	2.57	Ca(2)—O(3)	2.70
—O(7)—O(8)	2.65	—O(4)	2.59
—O(7)—O(16)	2.60	—O(5)	2.41
—O(8)—O(16)	2.81	—O(16)	2.87
		—HOH(1)	2.10
		—HOH(2)	2.45
		—HOH(3)	2.92

(Tables 5 and 6). Two more cycles of differential-synthesis refinement with partial aluminum added to these positions lowered the discrepancy index to .15.

Further refinement was made on an IBM 7040 computer with the Busing Martin and Levy least-squares refinement program.

Table 7. *Observed and calculated structure factors of yugawaralite*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	4	73.5	84.6	2	2	7	29.0	21.7	2	4	5	10.3	11.4	2	6	2	51.9	55.0
		6	79.1	88.9			8	2.6	6.4			6	10.6	7.5			3	22.1	23.7
		8	28.4	14.9			9	4.4	3.8			7	14.3	16.3			4	16.8	16.6
		10	12.8	13.9	3	2	0	32.9	29.8			8	21.8	23.3			5	8.4	5.5
1	0	4	72.4	77.3			1	24.6	8.2			9	12.9	9.7			6	4.7	6.5
		6	24.5	4.2			3	2.9	10.1	3	4	0	27.8	19.7			7	23.0	21.1
		8	8.2	8.3			4	25.5	24.0			1	11.5	21.9			8	7.1	3.5
		10	23.5	27.2			5	2.1	7.5			2	18.3	24.0	3	6	0	57.6	61.7
2	0	0	66.6	63.0			6	4.1	4.3			3	27.2	27.2			1	18.0	23.9
		2	6.8	7.9			7	22.5	15.1			5	9.9	4.7			2	9.6	10.4
		4	41.1	13.3			8	2.9	4.7			6	16.4	11.8			3	23.1	29.2
		6	54.2	53.2	4	2	0	34.5	32.2			7	20.3	26.4			4	33.1	29.6
		8	27.9	13.9			1	4.9	13.0			8	15.8	18.5			6	19.5	17.6
3	0	0	118.6	121.2			2	24.4	18.7	4	4	0	78.0	91.4	4	6	0	33.9	31.7
		2	27.2	22.7			3	5.2	7.8			1	34.0	39.0			1	15.8	16.9
		4	101.0	106.0			5	19.9	7.5			2	35.8	28.4			2	29.8	26.8
		6	33.0	30.6			6	17.7	15.1			3	7.7	9.2			3	24.4	9.5
		8	26.4	25.4	5	2	0	13.3	10.3			4	47.5	44.7			4	12.3	11.4
4	0	0	43.7	42.2			1	3.5	14.2			5	33.3	33.7			5	18.7	20.4
		2	69.4	72.9			2	34.5	34.9			6	26.0	22.1			6	7.8	11.9
		4	20.1	19.3			3	5.7	6.0	5	4	0	30.5	35.9	5	6	0	13.5	15.3
		6	19.8	23.4			4	22.8	25.2			1	5.3	10.0			1	9.9	8.0
5	0	0	41.4	50.6			5	16.8	12.6			2	57.6	59.6			2	18.9	17.8
		2	35.6	33.5	6	2	0	12.2	9.7			3	22.7	24.7			3	10.0	5.4
		4	34.4	31.4			1	2.9	10.0			4	40.5	40.1			4	8.1	6.7
6	0	0	54.1	67.3			2	12.6	10.6			5	9.0	5.9	6	6	0	14.6	18.3
		2	44.0	42.2			3	3.2	6.6	6	4	0	9.6	12.2			1	2.2	7.4
7	0	0	19.7	22.3	7	2	0	31.1	34.7			1	17.5	18.8			2	15.2	18.0
0	1	3	59.0	71.2	0	3	4	25.0	27.2			2	3.0	7.7	0	7	1	59.1	67.6
		4	23.4	13.1			5	27.5	28.5			3	15.9	13.7			2	20.8	19.3
		5	33.8	37.6			6	40.3	38.2	7	4	0	31.7	37.6			3	21.8	20.3
		6	66.0	68.7			7	37.7	40.1	0	5	2	36.8	37.8			5	17.4	14.7
		7	27.2	26.3			8	8.7	8.0			3	26.4	35.5			6	52.8	52.4
		8	23.1	16.0			9	5.8	13.0			4	27.4	37.9			7	23.9	24.0
		9	31.6	30.0			10	18.1	10.5			5	33.3	30.6			8	23.9	24.5
		10	38.6	41.2	1	3	2	39.3	35.2			6	8.0	4.2			9	19.4	25.0
1	1	2	29.5	29.5			3	40.5	34.4			7	41.9	46.9	1	7	1	21.2	21.8
		4	38.0	42.6			4	30.2	27.4			8	13.9	12.6			2	34.9	31.5
		5	33.3	29.3			5	23.8	27.8			9	7.4	12.4			3	33.4	32.2
		7	53.6	58.1			6	65.3	64.3			10	11.9	10.7			4	19.3	4.5
		8	32.9	29.8			7	25.0	23.3	1	5	0	38.4	37.4			5	28.3	24.6
		9	2.2	2.7			8	18.9	19.0			1	3.4	6.9			6	27.2	24.0
		10	4.5	4.9			9	8.6	2.3			2	27.4	23.3			7	14.9	15.8
2	1	0	22.8	26.8			10	25.4	27.1			3	13.7	13.7			8	45.0	40.1
		1	63.6	66.1	2	3	0	33.8	28.8			4	9.4	17.8			9	16.8	13.8
		2	23.6	13.3			1	44.0	39.1			5	17.5	10.5	2	7	0	7.3	7.6
		4	36.2	26.0			2	19.1	26.4			6	52.1	50.3			1	3.9	3.4
		5	20.1	20.6			3	37.7	31.0			7	7.2	8.1			2	34.3	17.6
		6	41.1	36.4			4	49.4	50.5			8	27.0	22.8			3	16.0	10.7
		7	6.1	8.5			5	41.9	42.3			9	5.8	16.2			4	19.4	8.2
		8	25.2	22.0			6	11.9	16.9	2	5	0	28.3	25.8			5	31.5	31.2
		9	2.6	3.6			7	23.4	13.6			1	28.4	27.1			7	11.8	10.2
3	1	0	3.2	8.2			8	55.0	50.0			2	27.3	31.5			8	19.0	18.2
		1	27.1	32.1			9	14.6	13.0			3	46.6	56.7	3	7	0	29.0	26.0
		2	30.9	29.7	3	3	0	27.1	21.0			4	26.7	23.2			1	31.7	35.1
		3	32.2	29.7			1	30.8	26.4			5	29.4	22.4			2	27.3	30.5
		4	57.5	43.8			2	12.7	14.2			6	27.3	24.4			3	25.1	19.5
		5	18.6	10.3			3	29.0	19.0			7	37.0	38.1			4	49.9	40.3
		6	30.6	38.6			4	19.8	16.6			8	17.5	19.0			5	22.0	27.8
		7	23.4	15.9			5	21.4	17.8	3	5	0	40.0	34.8			6	26.5	28.8
		8	21.5	20.4			6	31.1	18.3			1	55.1	55.0			7	10.1	13.7
4	1	0	3.0	10.1			7	9.1	6.1			2	35.2	33.4	4	7	0	10.0	5.5
		1	60.9	61.7			8	5.3	7.4			3	49.4	49.8			1	42.7	43.5
		2	21.8	16.3	4	3	0	27.2	26.8			4	12.7	16.0			2	31.4	27.8
		3	65.5	69.1			1	33.3	36.6			5	45.2	47.6			3	5.2	2.5
		4	3.8	10.9			3	28.8	28.4			6	13.2	12.4			4	12.2	20.0
		5	22.1	14.9			4	15.2	16.3			7	30.8	30.9			5	8.1	5.2
		6	34.6	27.1			5	24.1	19.0	4	5	0	21.3	17.4	5	7	0	14.3	11.3
		7	40.0	37.4			6	29.1	34.8			1	36.3	39.1			1	4.5	4.3
5	1	1	58.4	68.2	5	3	0	11.5	2.2			2	25.9	17.9			2	26.8	16.0
		2	4.9	8.8			1	31.8	39.9			3	25.3	19.1			3	9.6	8.3
		3	15.4	8.7			2	5.4	6.3			4	31.6	24.0			4	5.3	5.4
		4	2.6	6.6			3	20.2	8.3			5	24.2	17.5	6	7	0	29.8	26.1
		5	30.4	30.5			4	19.7	17.2			6	18.8	26.7			1	18.8	23.7
6	1	0	3.9	7.2			5	14.0	15.7	5	5	0	15.1	8.3	0	8	2	31.3	36.2
		1	16.2	21.1	6	3	0	17.0	16.3			1	2.6	13.2			3	12.7	15.3
		2	10.3	8.1			2	14.4	13.1			2	6.6	10.2			4	37.0	33.8
		3	3.5	2.7			3	6.8	9.2			3	24.4	21.6			5	44.5	44.8
7	1	0	19.8	17.4	7	3	0	24.2	22.5			4	6.3	5.9			6	48.5	46.2
		1	17.6	14.5	0	4	2	18.1	21.5	6	5	0	18.6	15.4			7	18.6	17.5
0	2	3	18.0	23.6			3	22.5	29.4			1	34.1	38.2			8	18.8	14.5
		4	24.9	14.1			4	2.1	3.1			2	13.7	16.2			9	7.0	8.0
		5	27.1	27.2			6	29.3	27.5	0	6	1	24.7	27.0	1	8	0	46.9	52.6
		6	6.8	11.6			7	27.4	20.9			3	11.7	18.3			1	37.4	40.1
		7	45.9	48.5			8	23.7	21.7			4	30.3	22.1			2	34.1	35.7
		8	22.4	9.5			9	14.6	14.1			6	17.8	20.5			3	12.1	2.5
		9	20.9	20.1			10	38.6	40.6			7	40.7	43.8			4	45.3	47.5
		10	18.3	14.3	1	4	0	191.8	184.3			8	21.6	19.1			5	19.8	20.1
1	2	2	63.5	76.2			3	39.4	31.7			10	3.9	6.5			6	28.5	32.6
		3	31.7	29.2			4	50.3	53.9	1	6	0	22.8	13.7			7	10.6	8.1
		5	22.4	14.3			5	43.8	45.5			1	26.3	17.2			8	17.9	20.0
		6	30.3	27.0			6	49.8	45.1			2	19.0	26.9	2	8	1	48.1	50.2
		7	43.7	41.3			7	23.6	9.2			4	22.5	21.7			2	10.0	8.6
		8	31.6	26.7			8	31.2	30.5			5	22.0	20.9			3	35.0	37.6
		9	20.6	10.2			9	19.1	20.5			6	12.2	18.2			4	29.0	20.8
		10	15.9	5.2	2	4	0	27.6	38.2			7	37.2	33.5			5	42.9	44.6
2	2	1	25.1	28.4			1	51.6	51.7			8	7.6	9.3			6	10.7	6.8
		3	17.5	18.3			2	86.8	101.7			9	5.2	7.5			7	41.7	38.8
		4	64.5	67.8			3	43.2	47.0	2	6	0	42.4	39.1	3	8	0	67.9	69.5
		6	24.2	23.7			4	71.8	72.9			1	37.2	33.4			1	26.9	26.3

Table 7. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	8	2	9.1	16.1	2	11	1	24.1	32.6	-2	0	2	41.0	37.0	-2	2	8	8.2	14.3
		3	47.0	51.7			2	14.0	9.4			4	48.5	51.3			9	18.9	19.6
		4	33.4	34.2			3	23.5	26.3			6	40.5	28.6			10	17.1	19.1
		5	48.1	46.2			4	7.9	1.4			8	32.4	34.1			11	2.6	5.3
		6	20.2	18.3			5	30.3	23.8			10	3.0	15.8	-3	2	1	2.5	7.4
4	8	0	7.5	7.0			6	7.8	8.6	-3	0	2	44.5	39.7			2	3.3	9.0
		1	26.1	29.8	3	11	0	17.9	14.4			6	45.7	47.2			3	20.8	20.7
		2	30.8	29.6			1	8.5	11.8			10	3.9	16.3			4	4.5	6.2
		3	26.1	19.0			2	18.1	19.0	-4	0	2	75.0	85.8			5	16.0	20.7
		4	35.1	32.4			3	10.0	8.5			4	17.3	12.0			6	3.0	3.3
		5	10.1	8.7			4	9.6	12.1			6	71.9	71.5			7	18.1	16.1
5	8	0	33.9	35.5	4	11	0	4.5	1.2			8	29.2	15.2			9	5.5	8.6
		1	24.0	24.0			1	5.2	10.4			10	48.3	52.9			10	3.3	11.9
		2	9.9	11.8			2	15.5	4.8	-5	0	2	24.3	31.8	-4	2	1	24.4	24.3
		3	21.3	17.4			3	3.9	3.2			4	3.1	9.0			3	35.0	35.8
6	8	0	13.1	18.3	5	11	0	13.4	13.4			6	55.9	54.2			4	16.0	7.4
		1	19.0	19.8			1	14.2	18.1			8	38.2	50.9			5	4.4	10.9
0	9	1	17.3	19.5	0	12	1	37.5	33.2			10	20.5	14.1			6	30.6	20.3
		2	7.7	16.4			2	28.4	32.0	-6	0	2	64.2	72.4			7	28.6	33.2
		3	16.8	13.0			3	16.2	15.5			4	22.0	22.3			8	18.7	13.6
		4	22.9	18.3			4	34.8	38.7			6	3.6	10.5			9	32.2	33.7
		5	17.6	15.2			5	17.3	12.3			8	3.0	3.1			10	27.4	28.8
		6	14.9	8.6			6	10.5	13.6			10	22.3	26.1			11	4.6	13.2
		7	10.7	10.8			7	6.2	6.9	-7	0	4	2.8	8.4	-5	2	1	24.1	25.0
		8	22.9	20.2	1	12	0	20.3	20.0			6	44.9	44.2			2	36.7	37.4
		9	21.2	19.0			1	44.6	46.1			8	16.3	10.8			3	14.3	6.4
1	9	0	44.5	42.2			2	7.2	5.3	-1	1	4	53.6	57.1			4	20.5	24.2
		1	35.8	36.9			3	19.5	21.4			5	29.9	26.8			5	18.7	18.8
		2	41.5	47.4			4	2.9	7.5			6	17.7	9.2			7	3.5	14.7
		3	68.9	71.5			5	29.9	26.9			7	16.8	19.2			8	3.4	10.0
		5	10.0	12.5			6	15.9	13.1			8	31.2	29.6			9	32.8	36.6
		7	32.4	34.7	2	12	0	18.7	21.0			9	16.6	14.9			10	9.8	9.2
		8	5.1	7.7			1	11.4	13.1			10	14.6	11.8			11	15.1	13.5
2	9	0	70.2	73.2			2	16.9	16.3			11	3.5	12.1	-6	2	2	29.0	32.7
		1	51.9	53.7			3	23.4	23.3	-2	1	2	44.3	45.3			3	15.2	14.5
		2	68.9	68.6			4	19.1	24.5			4	27.1	18.6			5	14.2	9.7
		3	46.3	47.8			5	18.0	17.7			7	41.4	46.3			6	4.1	3.7
		4	9.1	8.1	3	12	0	31.5	27.8			8	62.5	69.6			7	10.2	10.4
		5	16.4	14.0			1	9.3	9.2			9	7.4	3.9			8	14.1	14.9
		6	36.6	36.3			2	15.6	16.1			10	27.8	25.9			9	18.0	16.7
		7	13.7	13.4			3	14.6	8.6			11	1.3	3.1			10	4.3	2.5
3	9	0	14.7	18.2			4	22.8	23.5	-3	1	1	4.8	14.0	-7	2	1	6.6	8.3
		1	45.1	40.2	4	12	0	17.5	16.0			2	21.9	19.7			2	31.9	35.1
		2	16.7	16.8			1	19.2	17.2			4	66.2	67.8			3	14.6	21.9
		3	24.0	23.5			2	9.2	10.1			6	83.3	93.2			4	2.8	2.2
		4	17.5	23.5	0	13	1	13.5	17.9			7	24.0	23.8			6	5.6	4.0
		5	23.7	16.6			2	45.1	50.0			8	24.9	32.3			7	3.7	7.9
		6	19.7	18.3			3	24.8	24.0			9	31.3	34.6			8	12.8	3.7
4	9	0	14.6	13.4			4	26.3	31.0			10	36.8	34.9	-1	3	3	41.9	40.9
		1	25.3	28.4			5	9.6	12.2			11	3.4	5.4			5	31.8	33.3
		2	33.7	31.5			6	16.2	13.4	-4	1	1	25.9	16.2			6	37.2	38.0
		3	25.7	24.5	1	13	0	36.8	37.8			2	3.5	6.8			7	23.2	25.9
		4	23.3	25.8			2	23.6	17.4			3	34.4	29.8			8	61.1	65.7
		5	25.9	27.4			3	22.6	23.3			5	33.0	25.7			9	18.8	15.2
5	9	0	30.5	34.9			4	8.4	13.4			6	4.8	8.9			10	44.6	42.0
		1	27.9	29.5			5	3.8	8.5			7	5.1	8.1			11	26.4	21.6
		2	18.9	21.8	2	13	0	22.3	20.4			8	30.1	25.5	-2	3	1	10.4	4.4
		3	6.6	4.1			1	35.9	30.0			9	3.7	15.0			2	56.1	55.9
6	9	0	14.6	12.9			2	9.0	12.1			10	3.1	14.8			3	19.6	15.9
0	10	1	18.6	20.1			3	26.2	28.8			11	16.6	16.5			4	20.6	14.8
		2	19.0	18.1	3	13	0	31.6	32.2	-5	1	1	13.1	15.3			6	67.3	72.0
		3	15.4	15.2			1	13.5	16.1			2	2.2	3.7			7	34.6	38.7
		4	16.8	20.6			2	48.4	45.4			3	42.5	50.1			8	39.4	41.5
		7	16.1	10.4			3	8.0	8.2			4	43.4	41.1			9	22.2	18.5
		8	6.8	8.5	4	13	0	20.7	22.0			6	22.7	23.5			10	26.8	25.9
1	10	1	33.1	37.2			1	15.6	16.4			7	24.1	24.3			11	10.3	11.5
		2	49.4	41.8	0	14	1	17.9	20.2			8	16.2	16.0	-3	3	1	55.2	63.8
		3	14.3	21.3			2	25.3	20.6			9	3.6	10.3			2	41.3	44.5
		6	20.2	14.3			3	24.1	21.4			10	16.4	20.3			3	16.5	15.9
2	10	0	55.6	52.7			4	7.6	4.0			11	5.3	9.1			4	34.7	33.1
		2	11.9	8.6			5	29.3	29.1	-6	1	1	31.3	37.2			5	12.8	13.8
		3	22.8	24.9	1	14	0	14.7	13.3			2	38.6	45.2			6	41.2	39.2
		4	40.6	31.8			1	7.2	5.9			3	15.9	14.8			7	17.1	22.6
		5	22.3	20.9			2	6.1	7.1			4	24.2	26.5			8	21.1	15.7
		6	29.2	30.5			3	16.5	18.2			5	46.8	47.9			9	3.0	2.8
		7	20.9	17.6			4	22.1	23.9			6	27.5	29.8			10	10.5	9.5
3	10	0	9.2	7.6	2	14	0	7.6	13.4			7	2.5	3.2			11	11.3	9.1
		1	18.9	15.7			1	16.0	18.7			8	31.2	32.9	-4	3	1	7.8	16.1
		3	15.6	4.0			2	13.1	12.0			9	12.8	15.1			2	21.0	9.4
		4	17.9	13.5			3	13.8	10.1			10	17.0	16.4			3	25.3	24.7
		5	6.1	3.4	3	14	0	19.9	21.6	-7	1	1	3.4	5.4			4	65.9	73.8
4	10	0	32.9	36.8			1	14.2	16.6			2	13.6	8.0			5	20.7	9.9
		1	6.3	6.2			2	11.4	5.5			3	3.9	12.2			6	61.5	58.6
		2	9.8	11.7	0	15	1	20.4	16.8			4	23.0	27.1			7	60.7	63.6
		3	11.9	19.1			2	17.7	16.9			5	18.5	16.3			8	22.1	23.2
		4	12.2	7.5			3	19.2	15.2			6	23.3	28.3			9	7.1	8.0
5	10	0	9.4	9.5			4	17.1	18.7			7	2.5	12.2			10	36.0	34.7
		1	16.0	17.1	1	15	0	15.3	19.7			8	3.1	8.7			11	6.5	9.7
		2	21.1	20.1			1	18.9	15.1	-1	2	3	37.7	42.9	-5	3	1	28.2	22.0
0	11	1	20.7	15.3			2	16.2	18.6			7	39.9	40.5			2	43.5	51.2
		2	25.3	29.6			3	20.0	25.3			9	24.5	26.5			3	30.5	30.6
		3	36.8	38.1	2	15	0	28.3	31.4			10	5.3	11.0			4	35.1	42.8
		4	29.7	31.5			1	12.1	14.1			11	4.3	12.0			5	37.7	41.7
		5	14.7	8.8			2	15.6	16.0	-2	2	1	29.5	18.6			6	31.0	37.0
		6	12.7	3.0	0	16	1	5.0	8.0			2	105.2	103.6			7	19.0	19.8
		8	11.7	7.0			2	8.9	6.7			3	46.2	49.4			8	37.9	38.0
1	11	5	14.5	5.5	1	16	0	12.2	11.4			4	36.8	28.8			9	20.2	22.5
		6	28.5	27.2	-1	0	6	67.4	84.0			5	31.0	31.8			10	13.8	16.7
		7	23.1	18.7			8	17.5	19.9			6	24.3	24.4	-6	3	1	6.8	3.7
2	11	0	19.2	19.0			10	36.4	41.2			7	8.3	6.5			2	22.7	26.9

Table 7. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
-6	3	3	11.8	11.9	-2	5	6	34.0	33.3	-6	6	4	6.0	3.3	-4	8	5	8.4	11.1
		4	5.4	5.8			7	23.7	9.3			5	31.2	32.6			6	19.4	15.4
		5	16.7	15.6			8	28.3	32.7			6	7.4	7.1			7	44.4	35.3
		6	17.7	19.4			9	22.4	21.5			7	5.5	9.3			8	15.7	23.6
		7	9.4	8.7			10	9.4	9.5			8	6.5	6.9			9	6.0	5.2
		8	6.1	4.1			11	11.9	11.9			9	38.9	42.6	-5	8	1	9.6	8.9
		9	5.7	7.2	-3	5	1	28.7	36.9	-7	6	2	6.5	8.3			2	12.6	17.9
		10	10.1	9.4			2	12.6	9.4			3	2.8	3.9			3	18.8	13.0
-7	3	1	11.0	6.0			4	29.5	22.8			4	3.4	3.8			4	27.5	26.8
		2	11.6	13.3			5	5.3	1.5			5	7.4	10.8			5	20.4	22.2
		3	19.2	19.5			6	15.8	9.1			6	5.4	4.5			6	46.7	47.1
		4	25.9	28.4			7	54.4	54.2	-1	7	1	7.6	5.4			7	9.8	15.2
		5	6.9	2.7			8	24.3	24.9			3	23.2	23.7			8	11.7	11.7
		6	33.4	34.5			9	9.0	7.8			4	14.5	13.8			9	28.9	29.5
		7	14.1	18.5			10	3.2	0.6			5	26.5	30.5	-6	8	1	40.3	42.8
		8	8.7	11.0			11	5.2	11.8			6	42.5	35.8			2	37.0	38.3
-1	4	1	6.0	14.2	-4	5	1	22.8	30.4			7	35.1	34.2			3	11.5	11.0
		2	13.2	17.7			2	11.4	7.2			8	14.6	17.8			4	16.9	14.7
		3	15.1	14.3			3	45.4	48.6			9	17.3	19.9			5	13.0	10.2
		4	39.6	37.3			4	44.9	45.2	-2	7	1	42.7	49.7			6	14.4	14.3
		5	22.4	15.6			5	57.2	65.0			2	47.5	45.6			7	2.2	6.3
		6	35.5	37.9			6	68.2	68.3			3	15.2	19.9	-1	9	1	42.3	42.4
		7	23.0	24.8			7	13.7	14.6			5	7.9	7.2			2	33.4	62.5
		8	16.7	13.8			8	20.9	20.8			6	8.4	15.6			3	37.7	34.3
		9	20.5	22.4			9	33.1	30.1			7	25.1	17.4			4	26.2	30.4
		10	12.6	6.2			10	27.4	29.5			8	38.5	24.4			5	25.5	28.0
		11	21.0	11.0	-5	5	1	9.8	6.0			9	12.1	11.4			6	18.5	18.4
-2	4	1	33.4	36.6			2	33.1	36.4			10	25.9	27.2			7	24.9	25.6
		2	26.0	24.8			3	11.5	9.4	-3	7	1	32.5	35.5			8	3.2	3.3
		3	30.9	24.3			4	35.8	34.0			2	25.4	22.5			9	4.4	3.4
		4	12.1	10.5			5	11.6	14.5			3	22.5	29.6	-2	9	1	11.8	17.6
		6	31.8	32.4			6	4.2	5.6			4	36.1	24.2			2	39.5	42.9
		7	17.3	20.0			7	5.2	15.7			5	20.3	14.0			3	61.5	65.8
		8	39.9	40.7			8	44.2	46.7			6	65.7	67.8			5	17.9	16.0
		9	26.9	19.6			9	6.1	10.1			7	51.3	50.6			6	9.5	10.1
		10	17.2	15.4			10	16.7	16.7			8	18.5	11.3			7	48.0	53.8
		11	14.4	7.8	-6	5	1	11.7	12.3			9	10.7	10.2			8	3.6	4.5
-3	4	1	37.9	45.1			2	9.6	6.7			10	30.2	26.7			9	28.2	29.4
		2	30.1	29.9			3	39.8	43.6	-4	7	1	20.6	18.7	-3	9	1	9.3	12.8
		3	36.4	37.4			4	12.1	15.2			2	32.8	28.6			2	4.9	5.8
		4	13.7	12.8			5	6.1	5.8			3	28.4	29.0			3	39.6	40.0
		5	11.2	6.4			6	17.3	20.4			4	27.4	33.4			4	21.5	24.4
		6	35.8	36.5			7	29.3	33.0			5	44.9	45.1			5	53.0	52.5
		7	31.8	30.8			8	13.9	16.8			6	15.8	5.6			6	19.9	14.8
		8	10.5	10.3			9	5.9	13.4			7	10.2	13.3			7	14.3	14.8
		9	17.8	14.9	-7	5	1	27.0	29.4			8	19.4	22.6			8	27.4	34.0
		10	38.8	41.5			2	11.9	12.9			9	16.0	18.6			9	22.9	20.7
		11	13.0	12.5			3	17.0	22.3			10	20.8	18.6	-4	9	1	13.0	15.6
-4	4	1	15.4	8.1			4	8.1	5.2	-5	7	1	1.9	4.5			3	23.7	29.1
		2	19.6	17.0			5	39.3	38.2			2	33.1	35.7			4	21.6	22.0
		3	36.5	42.0			6	15.5	22.9			3	22.6	27.7			5	8.3	9.8
		4	48.1	49.7			7	17.4	16.7			4	29.6	33.2			6	17.9	19.8
		5	13.3	3.4	-1	6	1	49.7	41.0			5	4.5	6.1			7	12.3	14.2
		6	49.5	50.3			2	27.2	28.9			6	13.9	13.4			8	18.1	8.0
		7	21.8	14.9			4	21.2	9.4			7	6.6	11.6			9	8.9	10.7
		8	6.9	2.6			5	6.2	3.9			8	18.2	14.2	-5	9	1	14.7	14.2
		9	8.8	10.5			6	17.0	21.2			9	12.3	12.8			2	11.9	16.4
		10	15.0	11.5			7	27.0	24.0	-6	7	1	10.1	4.4			3	43.0	41.9
		11	11.3	8.9			8	13.6	14.3			2	28.0	33.2			4	10.5	15.4
-5	4	1	41.9	51.0			9	22.6	21.2			3	24.6	31.7			5	29.1	29.0
		2	62.0	67.8			10	20.8	19.3			4	24.9	20.6			6	13.4	12.4
		3	29.4	30.8	-2	6	1	17.5	19.6			5	2.2	4.8			7	19.5	18.7
		4	19.0	13.0			2	10.4	11.8			6	51.2	55.8			8	1.8	4.9
		5	26.5	28.4			4	54.0	57.6			7	20.1	21.8	-6	9	1	12.1	14.6
		6	31.0	32.6			5	35.4	41.3			8	28.1	24.4			2	13.7	13.1
		7	10.7	4.4			6	24.4	20.2	-7	7	3	6.5	7.5			3	7.7	4.8
		8	19.7	25.4			7	34.1	33.3			4	22.6	21.3			4	19.5	24.6
		9	14.6	17.9			8	4.5	10.0			5	19.8	22.0			5	21.9	20.5
		10	19.8	26.1			9	18.2	18.3	-1	8	1	40.3	42.8			6	4.2	8.6
-6	4	1	3.4	4.8			10	19.4	21.5			2	10.5	10.8	-1	10	1	19.9	18.7
		2	7.6	9.3	-3	6	1	45.3	45.2			3	29.0	31.5			2	13.2	12.5
		3	20.2	28.4			2	69.3	78.0			4	12.2	10.1			3	41.8	43.7
		4	5.1	5.1			3	19.3	18.7			5	35.3	41.9			5	34.3	34.8
		5	16.0	16.1			4	26.5	24.7			7	39.8	43.0			6	38.2	36.2
		6	44.0	46.7			6	21.5	24.4			8	28.7	23.0			7	21.3	23.9
		7	23.6	29.5			7	4.4	7.8			9	20.8	18.5			8	30.7	26.5
		8	21.3	22.0			8	28.9	23.3	-2	8	1	13.7	15.6	-2	10	1	48.8	52.2
		9	14.9	13.9			9	34.5	39.2			2	19.1	12.6			2	48.6	47.5
-7	4	1	8.6	5.4			10	7.7	2.9			3	26.8	16.4			3	10.3	10.2
		2	24.5	27.0	-4	6	1	12.8	7.5			4	36.3	39.3			4	10.5	9.6
		3	7.9	8.3			2	10.9	2.3			5	2.0	6.3			5	35.8	37.0
		4	14.2	12.7			4	13.8	10.9			6	46.0	45.2			6	17.2	14.6
		5	9.0	10.4			5	17.2	20.9			7	30.8	34.3			7	3.4	10.1
		6	13.3	13.1			7	18.3	3.9			8	11.8	18.1			8	20.5	14.6
		7	7.0	8.6			8	14.9	12.1			9	38.4	39.9			9	23.7	25.1
-1	5	1	25.2	27.1			9	9.9	13.4			10	18.7	20.2	-3	10	1	29.9	34.8
		2	21.4	17.4			10	12.0	17.6	-3	8	1	47.9	54.9			2	24.2	15.3
		3	34.0	33.8	-5	6	1	20.6	6.0			2	45.1	49.4			3	11.1	14.1
		4	21.8	16.5			2	19.3	19.0			3	22.1	19.1			4	24.9	19.9
		5	25.8	21.9			3	44.9	47.8			4	12.2	9.3			5	11.7	17.9
		6	11.5	15.4			4	30.7	29.0			5	38.1	43.2			7	15.0	13.0
		7	54.2	62.9			5	14.3	11.7			6	30.7	34.3			8	7.0	6.1
		8	20.4	19.5			6	18.3	17.6			7	3.0	9.5			9	7.0	3.4
		9	31.1	30.1			7	32.2	34.8			8	14.8	8.0	-4	10	1	33.7	33.6
		10	35.4	41.4			8	24.4	23.8			9	18.9	17.1			2	33.1	36.6
-2	5	1	45.8	46.8			9	15.2	17.6			10	8.5	16.2			3	6.5	7.2
		2	31.3	23.0			10	7.6	12.1	-4	8	1	37.3	37.0			4	20.9	4.6
		3	18.7	23.7	-6	6	1	21.0	27.2			2	16.8	19.6			5	18.9	18.9
		4	19.1	21.4			2	30.1	32.4			3	54.4	58.0			6	20.8	20.5
		5	8.7	12.1			3	9.0	9.2			4	11.3	8.7			7	13.6	9.0

Table 7. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
-4	10	8	43.7	45.4	-3	11	8	13.2	12.9	-3	12	7	35.6	28.7	-4	13	5	14.6	15.7
-5	10	1	14.2	16.0	-4	11	1	27.7	26.5	-4	12	1	6.0	9.0	-1	14	1	18.3	12.7
		2	16.6	15.3			2	19.8	11.2			3	12.8	7.0			2	18.9	14.8
		3	12.8	15.2			4	11.8	4.3			4	11.2	11.5			3	3.4	3.8
		4	14.0	7.4			5	28.0	26.9			5	5.6	8.9			4	18.6	13.4
		5	12.3	14.9			6	17.3	7.8			6	44.3	42.9			5	15.3	17.1
		6	5.5	5.8			7	18.8	7.3			7	3.6	8.1	-2	14	1	15.4	15.3
		7	17.2	16.2			8	5.0	4.9	-5	12	1	21.7	22.6			2	8.7	9.4
-6	10	2	19.1	18.0	-5	11	2	25.2	27.8			2	10.5	11.8			3	16.5	16.0
		3	7.1	10.3			3	17.7	24.5			4	11.5	11.2			4	31.0	24.1
		4	13.7	13.6			4	11.5	4.4			5	6.4	10.4			5	22.7	17.9
		5	14.4	11.5			5	11.4	5.1	-1	13	1	21.9	22.5	-3	14	1	33.7	33.0
-1	11	1	35.4	39.0			6	17.3	15.9			2	9.5	9.7			2	25.1	23.8
		2	28.1	32.0	-1	12	1	27.2	9.6			3	25.2	25.3			3	10.3	5.5
		3	32.8	36.4			2	18.4	22.6			4	9.8	11.1			4	9.0	9.2
		5	46.0	46.1			3	35.0	33.6			5	10.7	7.4			5	22.3	24.1
		6	12.2	14.3			4	25.1	23.9			6	15.8	14.5	-4	14	2	2.9	3.2
		8	13.6	7.5			5	15.2	19.1	-2	13	1	4.8	9.8	-1	15	1	4.3	3.2
-2	11	1	21.7	21.1			6	43.4	43.9			2	24.4	26.5			2	25.4	29.5
		2	26.3	19.3			7	11.1	6.7			3	25.5	25.0			3	14.5	9.8
		3	21.9	21.2	-2	12	1	40.0	43.2			5	4.4	12.0			4	2.1	2.9
		4	16.1	6.4			2	15.8	8.9			6	18.1	20.0	-2	15	1	14.3	10.8
		5	14.1	12.9			3	13.1	11.8	-3	13	1	3.6	7.1			2	12.0	5.3
		6	30.9	33.1			4	19.8	24.7			2	34.1	39.6			3	21.6	22.1
		7	48.9	52.2			5	41.0	43.8			3	23.3	23.8			4	3.2	9.6
		8	9.3	7.8			6	25.4	25.3			4	33.1	32.4	-3	15	1	21.3	25.1
-3	11	1	18.0	12.5	-3	12	1	9.8	6.8			5	5.4	4.3			2	4.7	8.2
		2	17.7	23.3			2	14.5	21.9			6	10.1	4.3	-1	16	1	7.6	1.9
		4	27.1	20.4			3	29.4	27.5	-4	13	1	6.2	8.5			2	22.6	19.2
		5	22.4	24.6			4	40.8	38.0			2	6.4	7.3					
		6	4.9	9.5			5	9.7	6.2			3	16.8	20.1					
		7	10.7	4.4			6	10.5	13.9			4	13.4	13.8					

A weighting scheme was devised by the authors using the following formula based on counting statistics:

$$\sigma(F) = \log\left[10^4 \cdot \sqrt{\frac{k \cdot Lp^{-1} \cdot Ab \cdot \sigma^2(I)}{4}}\right],$$

where k = scaling factor
Lp^{-1} = Lorentz-polarization factor
Ab = absorption correction factor
$\sigma^2(I)$ = relative variance in I
$= \sigma^2$(counting) + σ^2(time variation, etc.).

The weight assigned to each reflection was equal to $1/[\sigma(F)]^2$. Three cycles of least-squares refinement reduced the discrepancy index, R, from .15 to .14, and to a weighted R of .13.

Table 5 lists the final atomic coordinates, standard deviations, site occupancies, and temperature factors for all the independent atoms in the yugawaralite structure. Table 6 lists the interatomic distances for atoms in the structure. Table 7 lists observed and calculated structure factors.

Discussion of the structure

The tetrahedral framework

The crystal structure of yugawaralite is characterized by four-membered ring groups of silica-alumina tetrahedra approximately perpendicular to the c axis, by five-membered ring groups at about

65° to either side of the *ac* plane, and by eight-membered ring groups which form channels parallel to the *a* and *c* axes. The axes of these channels lie on planes parallel to the *ac* plane at distances of .25 and .75 on the *b* axis. This places the channels between the glide planes of the space group.

Figure 4, a schematic drawing of part of the framework viewed parallel to the *a* axis, shows the concentration of silica tetrahedra in planes parallel to the *ac* plane al distances of approximately .00 and .50 on the *b* axis and the relatively few oxygen atoms which serve to

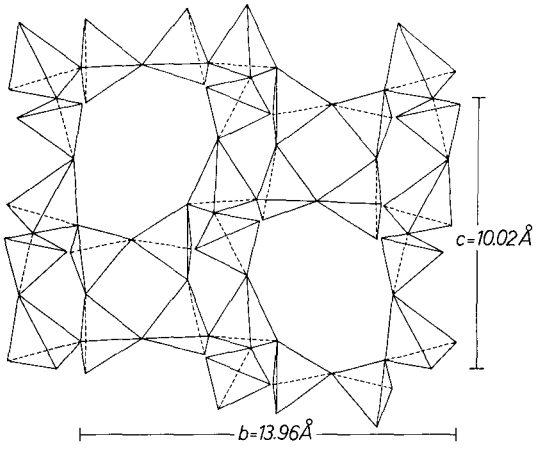

Fig. 4. Schematic drawing of part of the framework viewed parallel to the monoclinic *a* axis of yugawaralite showing four- and five-membered ring groups and the (010) cleavage

bond these adjacent layers, forming the (010) cleavage of yugawaralite. Figure 4 also shows one set of unrestricted eight-membered ring channels held together by a complex linking of four- and five-membered ring groups.

Figure 5, a schematic drawing of part of the framework viewed parallel to the *b* axis, shows the complex linking at four- and five-membered ring groups in one plane of concentration of silica tetrahedra parallel to the *ac* plane. The complex linking accounts for the absence of layering in this plane and the absence of relatively few bridging oxygen atoms which would lead to (100) or (001) cleavage.

Figure 6, a schematic drawing of part of the framework viewed parallel to the *c* axis, shows a four-membered ring group approxi-

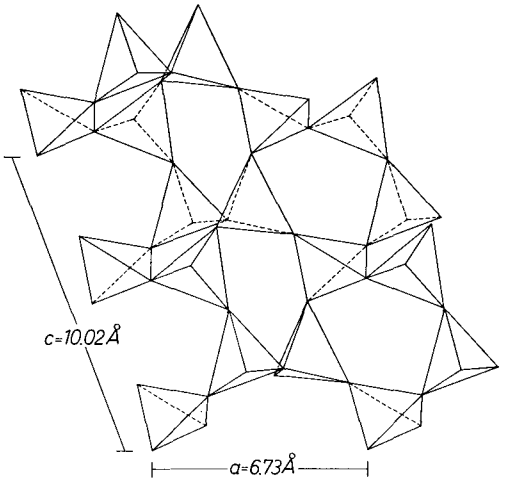

Fig. 5. Schematic drawing of part of the framework viewed parallel to the monoclinic *b* axis of yugawaralite showing five-membered ring groups

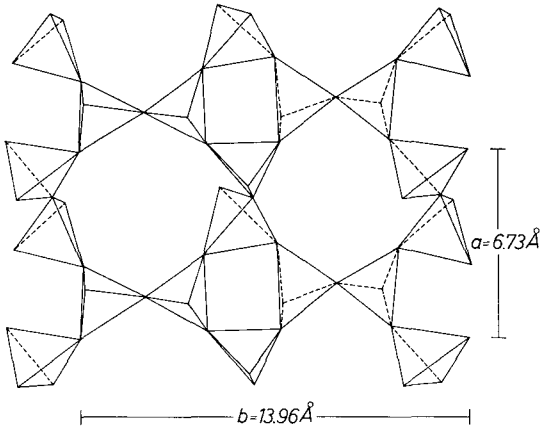

Fig. 6 Schematic drawing of part of the framework viewed parallel to the monoclinic *c* axis of yugawaralite showing four- and eight-membered ring groups and the (010) cleavage

mately perpendicular to the *c* axis. The two tetrahedra of this group lying in a plane parallel to the *bc* plane can be referred to as the "up-down" tetrahedra linkage of SMITH and RINALDI (1962). The other two tetrahedra have been twisted such that one of the remaining two vertices "points" up and the other down. Also shown is the set

of unrestricted eight-membered ring channels parallel to c and bounded by four-membered ring groups. The (010) cleavage plane bisects both sets of eight-membered ring channels at $b = .25$ and .75.

As stated by ZOLTAI and BUERGER (1960) the relative energy of five- and six-membered tetrahedral rings is low, thus favoring their stability over other types of tetrahedral ring arrangements. The presence of numerous four-membered tetrahedral rings in the structure accounts for the relative rarity and instability of yugawaralite in nature.

Substitution of aluminum for silicon

During differential-synthesis refinement, the electron densities, curvatures, and temperature factors of four independent silicon atoms became noticeably different from the other four independent silicon atoms. Oxygen atoms associated with these four silicon positions have greater than normal Si—O bond distances (Table 6). These sites are considered to be partially occupied by aluminum.

Assuming a linear increase in mean tetrahedral distance with increasing percentage aluminum from 1.61 Å for 0% Al to 1.75 Å for 100% Al (SMITH and BAILEY, 1963), there is 60% substitution of Al for Si in tetrahedral sites 2 and 7 and 40% substitution in sites 3 and 5. The amount of substitution of the tetrahedral sites agrees well with the partial occupancy of the calcium sites derived from differential-synthesis refinement. All calcium atoms are associated with oxygen atoms in aluminum-substituted tetrahedra. The close association of calcium with oxygen in aluminum-substituted tetrahedra is consistent with PAULING's electrostatic-valence rule (1960).

Although tetrahedral sites 2 and 3 are adjacent as are sites 5 and 7, there need be no violation of the Al—O—Al avoidance rule since these are partially occupied positions. When sites 2 and 7 are occupied 3 and 5 are not, and vice versa.

Cation-water-framework relationships

Calcium is distributed on two general positions occurring in the open channels near the intersection of the eight-membered rings. The relationship between the calcium, framework, and water molecules is shown in Fig. 7.

Calcium atom 1 is coordinated to four framework oxygen atoms from aluminum-substituted tetrahedra and four water molecules which occupy general positions in the channels. Calcium atom 2 is coordinated to four framework oxygen atoms and three water molecules. It is suspected that another water molecule is present in the coordination of calcium 2, but it could not be placed from difference

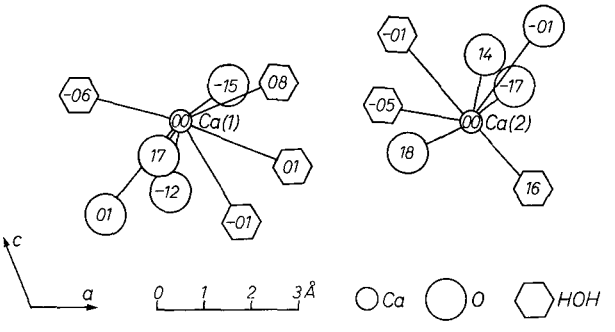

Fig. 7. Environments surrounding each of the calcium positions in yugawaralite. The number on each atom is its y coordinate

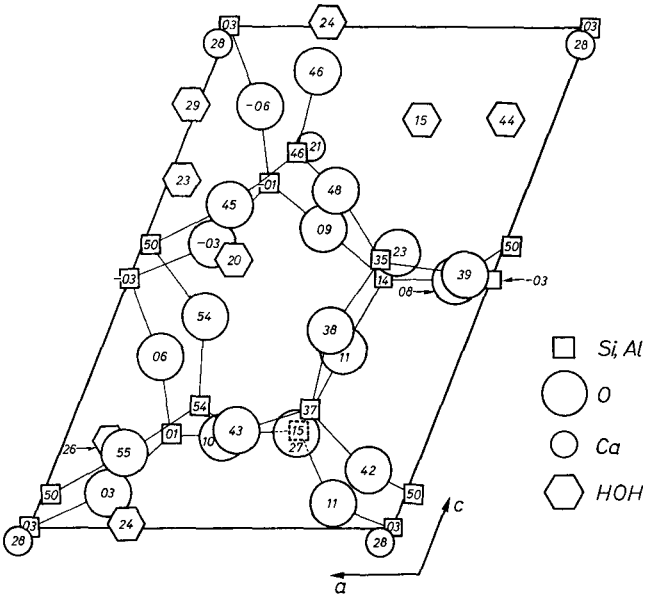

Fig.8. Projection of all atoms in the half cell of yugawaralite on the (010) plane. The number on each atom is its y coordinate

Fourier synthesis. An additional water molecule bonded to calcium atom 2 would give both calcium atoms eightfold coordination. Since the calcium atoms are unequally distributed, not all water sites have full occupancy. Because the calcium atoms are closely associated with aluminum-substituted silica tetrahedra, they occur near the sides of the open channels rather than in the middle (Figs. 8 and 9). All the coordinated water molecules lie at about the same distance from the calcium atom, implying that they are bound equally to the calcium atoms.

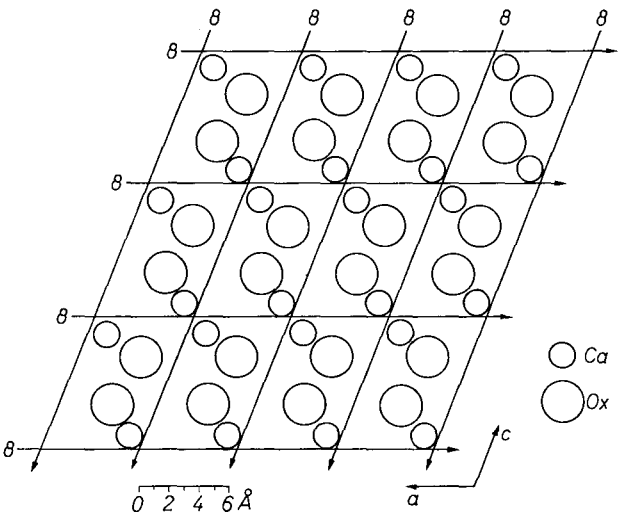

Fig. 9. Map view of atoms on the (010) plane in yugawaralite showing channel directions, number of tetrahedra in each ring forming the channels, and the positions of the calcium ions in the channels

Figure 9, a map view of the (010) plane, shows all channel directions and indicates the number of tetrahedra that comprise the rings forming these channels. Calcium atoms are shown in the proper positions near, but not at, the intersections of the axes of the channels.

Channel dimensions in yugawaralite are calculated using the coordinates of oxygen atoms forming each channel, an oxygen radius of 1.40 Å, and the unit-cell dimensions. Both sets of eight-membered ring channels have effective diameters of approximately 3.7 Å. On this basis it is predicted that yugawaralite would not be a good material for molecular sieves or water softeners. It could exchange its cations with similar cations slowly and perhaps incompletely.

Relationship of differential thermal analysis to the structure

The determination of the crystal structure of yugawaralite leads to a more complete interpretation of the differential thermal analysis pattern. This pattern (Fig. 2*a*) shows two prominent endothermic peaks occurring in the temperature ranges of 80° to 100 °C and 380° to 420 °C, each associated with water loss. The first endothermic peak represents the loss of absorbed and adsorbed water below 100 °C. Since all the water molecules are coordinated equally to each calcium atom, all are probably bonded equally. The second endothermic peak represents the loss of all the structurally bonded water molecules.

Relationship to other zeolites

Yugawaralite has characteristics in common with a few of the other zeolites, but it does not have enough in common with any of the seven structural groups described by SMITH (1963) or MEIER (1967) to place it in one of them. Although yugawaralite has five-membered rings, the structure is not based on a columnar arrangement of these five-membered rings as in mordenite. In yugawaralite these five-membered rings are combined with four-membered rings to form infinite layers parallel to the *ac* plane which are bonded together by a relatively small number of oxygen atoms. The characteristic 7.5 Å spacing for a five-membered ring is masked by the fact that the plane formed by the ring is not parallel to any of the axial planes but at an angle.

Members of the phillipsite group and yugawaralite have structures which are based upon interconnected four-membered rings. In this

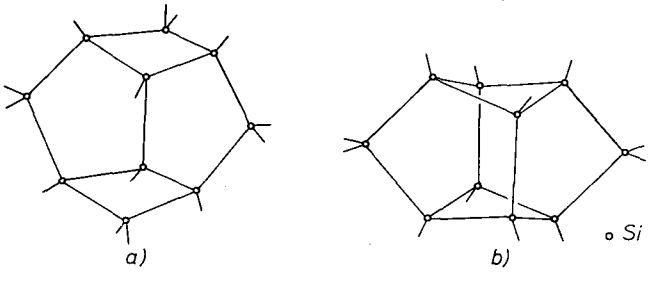

Fig. 10. Comparison of the common structural feature of (*a*) yugawaralite and (*b*) heulandite group

group, however, adjacent tetrahedra of the four-membered rings lie in planes approximately parallel to axial planes, whereas in yugawaralite, adjacent tetrahedra lie in planes on a diagonal to the axial planes.

The common structural feature of yugawaralite is most similar to those of the heulandite group (MEIER, 1967), but they are not enough alike to place yugawaralite in this group (Fig. 10). Since yugawaralite does not have enough characteristics in common with any of the previously defined structural groups of zeolites to place it in one of them, it is suggested that an eighth group be created which would contain these new linkages.

Acknowledgments

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