

## Lattice constants of wairakite as a function of chemical composition

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### Abstract

Fourteen natural wairakite specimens from Japan were studied to evaluate the relationship between their lattice constants and their chemical composition. The lattice constants were determined using *hkl* indices which were assigned on the assumption that the monoclinic lattice of wairakite is closely related to that of analcime. Examination of the extinction rules indicated either *Ia* or *I2/a* as the possible space groups. Multicomponent regression analyses were carried out to evaluate the relationship between the chemical composition and the lattice constants. The parameters *a*, *b*, *c*,  $\beta$ , and *V* are expressed in terms of the numbers of sodium and silicon atoms and water molecules per unit cell as follows:

$$a (\text{\AA}) = -0.0040 \text{ Na} - 0.0015 \text{ Si} - 0.0036 \text{ H}_2\text{O} + 13.8058$$

$$b (\text{\AA}) = 0.0075 \text{ Na} + 0.0009 \text{ Si} + 0.0021 \text{ H}_2\text{O} + 13.5723$$

$$c (\text{\AA}) = 0.0148 \text{ Na} + 0.0021 \text{ Si} + 0.0061 \text{ H}_2\text{O} + 13.3745$$

$$\beta (^\circ) = -0.0939 \text{ Na} + 0.0262 \text{ Si} + 0.0086 \text{ H}_2\text{O} + 89.6046$$

$$V (\text{\AA}^3) = 3.6122 \text{ Na} + 0.1580 \text{ Si} + 0.7724 \text{ H}_2\text{O} + 2511.8682$$

The magnitudes of the standard deviations of the individual coefficients indicate that only the sodium content can be effectively predicted from the lattice parameters. The number of sodium atoms per unit cell can be estimated by the following equation:

$$\text{Na} = -15.8748(a - c) - 16.4222(a - b) - 3.3825\beta + 310.0658 \pm 0.2495$$

Another equation which can be used for this purpose is based upon the observed values of  $2\theta^\circ$  for  $\text{CuK}\alpha_1$  radiation:

$$\text{Na} = -10.833 \{2\theta^\circ(004) - 2\theta^\circ(400)\} - 8.933 \{2\theta^\circ(040) - 2\theta^\circ(400)\} + 4.640 \pm 0.2832$$

### Introduction

Wairakite ( $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ ) is generally recognized as the calcium analogue of analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ) since the first description by Steiner (1955) and Coombs (1955). Many researchers have discussed the mutual solid solubility of these minerals [Harada and Nagashima (1972), Harada and Sudo (1976), Seki and Oki (1969), Seki (1971a,b), Surdam (1967)]. However, the mineralogical properties of intermediate members in the series are not well known, probably because it is very difficult to obtain accurate crystallographic data. This difficulty is caused mainly by the polysynthetic twinning and pseudocubic character of the lattice.

This study aims at clarification of the mineralogical properties of the calcium-rich members of the series. The relationship between the lattice constants and the chemical composition of the calcium-rich species has been established from powder diffraction data with higher resolution than that used in previous works.

Wairakite is commonly found in geothermal areas and its Na-Ca ratio appears to be a function of parameters such as temperature and chemical composition of the hydrothermal solution. Therefore the determination of the chemical composition of members of the series between wairakite and analcime is applicable to geochemical investigation of the hydro-

thermal alteration. The relation between the lattice constants and chemical composition obtained in this work provides an indirect determinative method of the sodium content of wairakite.

### Experimental procedures

Chemical analyses and X-ray diffraction studies were carried out on fourteen wairakite specimens from Japan. Brief notes on the localities and on their modes of occurrence are given in the footnotes to Table 1.

Chemical compositions were determined as follows: about 300 mg of powdered material was divided into three fractions. The first fraction was decomposed with HF and H<sub>2</sub>SO<sub>4</sub> and the contents of Na<sub>2</sub>O, K<sub>2</sub>O, MgO, CaO, and Fe<sub>2</sub>O<sub>3</sub> were determined by means of atomic absorption spectroscopy. The second fraction was decomposed by fusion with Na<sub>2</sub>CO<sub>3</sub> and the amounts of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were determined by gravimetric methods. The amount of H<sub>2</sub>O was determined by means of thermogravimetry on the third fraction of the material.

X-ray powder diffraction data were obtained on a Rigaku-Denki low-angle diffractometer using Ni-fil-

tered CuK $\alpha$  radiation at 30 kV and 15 mA. For the experiments about 10 mg or less of the powdered specimen was spread into a thin film on a sample holder of single-crystal quartz. A scanning speed of 0.25° 2 $\theta$  per minute and a slit system of 1-0.4-0.1 for the reflections 400, 040, 004,  $\bar{3}32$ ,  $\bar{2}33$ , and 332 and of 1-1-0.2 for other reflections were used. Silicon was used as an internal standard, and the lattice constants were obtained by means of a least-squares method using 35 sharp reflections for each sample.

### Results and discussion

The results of the chemical analyses are shown in Table 1, together with the numbers of ions and water molecules per unit cell on the basis of 96 oxygens in the framework. The term C.B.% refers to the charge balance between the negative charge in the framework and the positive charge of the cations and is defined as follows:

$$\text{C.B.\%} = [2(\text{Ca} + \text{Mg}) + \text{Na} + \text{K} - (\text{Al} + \text{Fe})]/(\text{Al} + \text{Fe}) \times 100$$

This term indicates the analytical error, the degree of

Table 1. Chemical composition of wairakite

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.
SiO <sub>2</sub>	52.00	54.20	54.35	54.52	54.46	54.23	54.70	54.52	56.45	55.91	55.30	54.49	55.23	56.50
Al <sub>2</sub> O <sub>3</sub>	25.21	24.35	23.95	23.85	23.92	24.23	24.00	23.81	22.90	22.98	23.09	23.76	23.33	22.00
Fe <sub>2</sub> O <sub>3</sub>	0.44	0.15	0.10	0.10	0.04	0.45	0.05	0.09	0.14	0.13	0.09	tr.	tr.	0.11
MgO	0.27	tr.	0.05	0.13	tr.	0.15	0.03	0.01	tr.	0.04	0.02	tr.	tr.	0.04
CaO	13.09	12.73	12.85	12.40	12.94	12.33	12.46	12.41	11.49	11.90	12.03	11.50	11.92	10.25
Na <sub>2</sub> O	0.18	0.21	0.21	0.25	0.26	0.29	0.39	0.48	0.82	0.96	1.04	1.25	1.35	1.88
K <sub>2</sub> O	0.25	0.02	0.22	0.34	0.04	0.04	0.08	tr.	tr.	0.07	0.03	0.11	tr.	0.08
H <sub>2</sub> O	8.78	8.60	8.57	8.51	8.46	8.47	8.53	8.52	8.45	8.33	8.50	8.57	8.50	9.15
Total	100.22	100.26	100.30	100.10	100.12	100.19	100.24	99.84	100.25	100.32	100.10	99.68	100.33	100.01
Numbers of ions and water molecules per unit cell														
Si	30.486	31.456	31.568	31.688	31.648	31.464	31.704	31.824	32.536	32.272	32.104	31.784	32.000	32.904
Al	17.388	16.627	16.637	16.307	16.322	16.538	16.365	16.304	15.526	15.606	15.772	16.306	15.901	15.072
Fe	0.292	0.066	0.044	0.044	0.018	0.096	0.022	0.040	0.061	0.056	0.038	0.000	0.000	0.035
Mg	0.236	0.000	0.086	0.226	0.000	0.130	0.026	0.012	0.000	0.035	0.014	0.000	0.000	0.048
Ca	8.223	7.917	7.998	7.722	8.042	7.665	7.738	7.739	7.095	7.360	7.485	7.219	7.399	6.395
Na	0.204	0.236	0.236	0.282	0.292	0.326	0.438	0.538	0.914	1.073	1.164	1.411	1.514	2.119
K	0.188	0.014	0.162	0.252	0.030	0.030	0.060	0.000	0.000	0.051	0.021	0.082	0.000	0.059
H <sub>2</sub> O	17.158	16.639	16.594	16.486	16.356	16.380	16.480	16.530	16.233	16.029	16.449	16.665	16.414	17.760
C. B. %	-1.59	-3.30	-0.42	-0.93	-0.39	-5.96	+2.27	-1.91	-3.20	+1.57	+2.30	-2.36	+2.52	-0.55

1-6,9,10,12-14: Seigoshi mine, Toi, Shizuoka Pref., Japan. Occurs in veins of 1-30 mm thick in altered andesite and andesitic pyroclastics which belong to Miocene or younger age, sometimes associated with laumontite, scolecite, stilbite, chabazite, epidote, calcite and quartz.

7: Ikadaba, Kawazu, Shizuoka Pref., Japan. Occurs in druses in Miocene andesitic pyroclastics as euhedral crystals up to 8 mm in diameter, sometimes associated with calcite.

8,11: Bandaiatami, Koriyama, Fukushima Pref., Japan. Occurs in veins of 10-100 mm thick in Miocene andesitic pyroclastics, sometimes associated with epidote, prehnite, stilbite, calcite and quartz.

the contribution of hydronium ions, and/or the presence of other chemical species for which chemical analyses were not made.

The lattice constants and their standard deviations are listed in Table 2. X-ray powder data for sample No. 4 are shown in Table 3. The intensities listed in the table represent peak heights, because many reflections are so closely spaced that accurate determinations of true intensities of the individual reflections are impossible.

From the striking morphological similarities and similar powder diffraction patterns, it has generally been accepted that the crystal structures of wairakite and analcime are alike. The  $hkl$  indices in this study have been assigned on the assumption that wairakite has a monoclinic lattice which is slightly different from that of analcime. The results of the examination of the extinction rules are as follows: The reflections of the type ( $hkl$ ) are extinguished where  $h + k + l = 2n + 1$ , and the reflections of the type ( $h0l$ ) are extinguished where  $h$  or  $l$  are odd. These conditions indicate  $Ia$  or  $I2/a$  as possible space groups.

Multicomponent regression analyses were carried out to determine the relations between the lattice constants and the chemical composition. Usually wairakite is mainly composed of eight components: CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O. As a first approximation MgO, K<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub> can be neglected because their amounts are very small. From the valency balance of the wairakite structure, the mode of substitution can be expressed as follows:  $(Ca, Na_2)Al_2 \rightleftharpoons Si_2$ . Therefore only three among five major components are independent of each other. The contents of Na<sub>2</sub>O, SiO<sub>2</sub>, and H<sub>2</sub>O

were chosen as variables in the first-order regression equations. The lattice constants are expressed in terms of the numbers of sodium and silicon atoms and water molecules per unit cell as follows:

$$a (\text{\AA}) = -0.0040Na(\pm 0.0025) - 0.0015Si(\pm 0.0025) - 0.0036H_2O(\pm 0.0024) + 13.8058(\pm 0.1021)$$

$$b (\text{\AA}) = 0.0075Na(\pm 0.0024) + 0.0009Si(\pm 0.0024) + 0.0021H_2O(\pm 0.0023) + 13.5723(\pm 0.0958)$$

$$c (\text{\AA}) = 0.0148Na(\pm 0.0030) + 0.0021Si(\pm 0.0030) + 0.0061H_2O(\pm 0.0028) + 13.3745(\pm 0.1190)$$

$$\beta (^\circ) = -0.0939Na(\pm 0.0196) + 0.0262Si(\pm 0.0196) + 0.0086H_2O(\pm 0.0186) + 89.6046(\pm 0.7887)$$

$$V (\text{\AA}^3) = 3.6122Na(\pm 0.8682) + 0.1580Si(\pm 0.8671) + 0.7724H_2O(\pm 0.8202) + 2511.8682(\pm 34.8098)$$

The numbers in parentheses correspond to the standard deviations of the regression coefficients. These equations show that an increase of the sodium content results in an increase of  $b$ ,  $c$ , and  $V$  and in a decrease of  $a$  and  $\beta$ . The influence of either silicon or water content is rather indistinct except for the positive correlation of silicon with  $\beta$  and of water with  $c$ . The magnitude of the standard deviations may result from a fourth factor, such as the degree of ordering of silicon and aluminum atoms in the framework, and may also reflect the heterogeneity of the samples and/or uncertainties of the individual determinations.

When the regression coefficients are compared with the magnitude of their standard deviations, it is obvious that the effects of sodium content on the lattice constants are most distinct. First- and second-or-

Table 2. Lattice constants of wairakite

Sample No.	$a_o$ (Å)	$b_o$ (Å)	$c_o$ (Å)	$\beta_o$ (°)	$V_o$ (Å <sup>3</sup> )	$a_o - c_o$ (Å)	$a_o - b_o$ (Å)
1.	13.7003(19)	13.6377(11)	13.5449(11)	90.54(3)	2530.6(8)	0.1554	0.0626
2.	13.6986(11)	13.6403(7)	13.5461(7)	90.51(2)	2531.0(5)	0.1525	0.0583
3.	13.6969(26)	13.6355(19)	13.5447(15)	90.55(5)	2528.9(11)	0.1522	0.0614
4.	13.6947(27)	13.6377(17)	13.5498(16)	90.55(5)	2530.5(11)	0.1449	0.0570
5.	13.7018(23)	13.6346(13)	13.5408(12)	90.56(4)	2529.5(9)	0.1610	0.0672
6.	13.7021(22)	13.6393(12)	13.5502(13)	90.55(3)	2532.2(9)	0.1519	0.0628
7.	13.6998(15)	13.6375(8)	13.5471(8)	90.55(3)	2530.9(6)	0.1527	0.0623
8.	13.6950(17)	13.6386(11)	13.5553(11)	90.50(3)	2531.8(7)	0.1397	0.0564
9.	13.6977(41)	13.6402(16)	13.5534(18)	90.54(7)	2532.2(14)	0.1443	0.0575
10.	13.6993(28)	13.6457(13)	13.5530(14)	90.48(4)	2533.5(10)	0.1463	0.0536
11.	13.6967(14)	13.6512(9)	13.5640(7)	90.44(2)	2536.1(6)	0.1327	0.0455
12.	13.6960(36)	13.6456(20)	13.5610(27)	90.47(12)	2534.3(15)	0.1350	0.0504
13.	13.6878(35)	13.6446(22)	13.5679(22)	90.43(15)	2533.9(15)	0.1199	0.0432
14.	13.6860(39)	13.6554(27)	13.5836(36)	90.42(17)	2538.5(19)	0.1024	0.0306

Table 3. X-ray diffraction powder data for wairakite (for No. 4 specimen)

hkl	d(calc.)	d(obs.)	I/I <sub>0</sub>	hkl	d(calc.)	d(obs.)	I/I <sub>0</sub>	hkl	d(calc.)	d(obs.)	I/I <sub>0</sub>
200	6.847			244	2.272	2.274	1	237	1.729		
020	6.819			244	2.263			156	1.727		
121	5.574			424	2.261	2.261	1	165	1.726	1.727	7
112	5.565			323	2.213			237	1.720		
211	5.559	5.560	80	161	2.213			516	1.720	1.720	6
121	5.556			253	2.213			327	1.719		
220	4.832	4.828	23	161	2.212	2.212	8	080	1.707	1.705	3
123	3.634			532	2.211			008	1.694	1.693	2
132	3.634	3.630	18	352	2.210			741	1.685	1.685	1
312	3.633			235	2.198	2.199	2	741	1.682	1.681	1
400	3.424	3.423	41	026	2.144	2.143	3	471	1.681		
040	3.409	3.409	47	514	2.114	2.115	3	471	1.679		
004	3.387	3.386	100	145	2.094	2.092	1	417	1.679	1.678	1
411	3.232			415	2.090			174	1.677		
330	3.221	3.226	1	226	2.051	2.051	2	174	1.675	1.674	2
411	3.218			136	1.998			714	1.674		
141	3.216	3.217	1	316	1.995	1.998	3	147	1.672	1.671	1
033	3.204			444	1.961	1.960	1	147	1.669		
114	3.203	3.203	1	550	1.933	1.933	1	417	1.665	1.666	1
402	3.067	3.067	4	640	1.897	1.896	2	118	1.666		
204	3.048			460	1.894			820	1.660	1.660	1
042	3.045	3.045	5	406	1.893	1.893	4	280	1.654	1.655	1
402	3.044			064	1.887	1.888	4	356	1.629		
204	3.025	3.025	1	604	1.884	1.885	4	653	1.628	1.629	1
332	2.917			046	1.883	1.883	2	563	1.628		
323	2.916	2.916	39	712	1.867			660	1.611	1.610	1
233	2.910	2.911	34	721	1.865	1.866	2	822	1.609		
332	2.901	2.901	23	633	1.865			228	1.595	1.595	2
233	2.894			363	1.858			813	1.595		
323	2.893	2.894	26	712	1.857			831	1.589	1.590	2
224	2.782	2.782	5	271	1.857			473	1.588		
224	2.765	2.765	5	172	1.856	1.855	7	381	1.585		
341	2.681			336	1.855			813	1.585		
314	2.679	2.679	8	172	1.854			183	1.585	1.585	3
431	2.677			633	1.853			183	1.584		
512	2.504	2.505	2	336	1.843	1.843	2	743	1.584		
512	2.488			642	1.823			347	1.584		
152	2.486	2.487	17	264	1.822	1.823	1	318	1.582		
215	2.486			246	1.819	1.819		734	1.582		
440	2.416	2.416	8	723	1.742	1.742	2	374	1.581	1.581	2
530	2.346			732	1.741			075	1.582		
350	2.341	2.343	2	372	1.731						
035	2.328	2.330	1	723	1.730						
442	2.280			327	1.730	1.729	10				
424	2.280	2.281	3	273	1.729						

der regression analyses were also carried out to determine the relation between the lattice constants and analcime molecule  $X_{Am}$ , which is defined using the numbers of ions per unit cell as follows:  $X_{Am} = Na/[Na + K + 2(Mg + Ca)]$ . Resultant regression equations and standard deviations of fitting are as follows:

$$\begin{aligned}
 a(\text{\AA}) &= -0.0366 X_{Am} + 13.6991 \pm 0.0038 \\
 a(\text{\AA}) &= 5.0090 X_{Am}^2 - 0.7055 X_{Am} + 13.7250 \pm 0.0107 \\
 b(\text{\AA}) &= 0.1422 X_{Am} + 13.6347 \pm 0.0027 \\
 b(\text{\AA}) &= -0.1446 X_{Am}^2 + 2.0751 X_{Am} + 13.5961 \pm 0.0989 \\
 c(\text{\AA}) &= 0.2963 X_{Am} + 13.5401 \pm 0.0039 \\
 c(\text{\AA}) &= -6.7378 X_{Am}^2 + 1.1962 X_{Am} + 13.5221 \pm 0.0145 \\
 \beta(^{\circ}) &= -1.1248 X_{Am} + 90.5608 \pm 0.0244 \\
 \beta(^{\circ}) &= 7.3701 X_{Am}^2 - 2.1091 X_{Am} + 90.5805 \pm 0.0268
 \end{aligned}$$

$$V(\text{\AA}^3) = 61.2639 X_{Am} + 2529.4593 \pm 1.0391 \dots\dots (*)$$

$$V(\text{\AA}^3) = 388.9004 X_{Am}^2 + 9.3236 X_{Am} + 2530.4984 \pm 18.4821$$

Judging from the magnitude of the standard deviations of fitting, the lattice constants can be better approximated by linear functions of  $X_{Am}$  than by quadratic ones.

The unit-cell volume of individual specimens and the regression line are shown in Figure 1. When the cell volume of analcime is estimated by the linear equation (\*), we obtain  $V(\text{\AA}^3) = 2590.72 \pm 1.04$ . The average Si/Al ratio for the specimens used in this work is about 1.97. Among the already published data on the cell volume of analcime having Si/Al ratios higher than 1.97, the maximum value is  $2586.6\text{\AA}^3$ , which was reported by Mazzi and Galli (1978). The value extrapolated by the equation is significantly larger than this value. The compositional

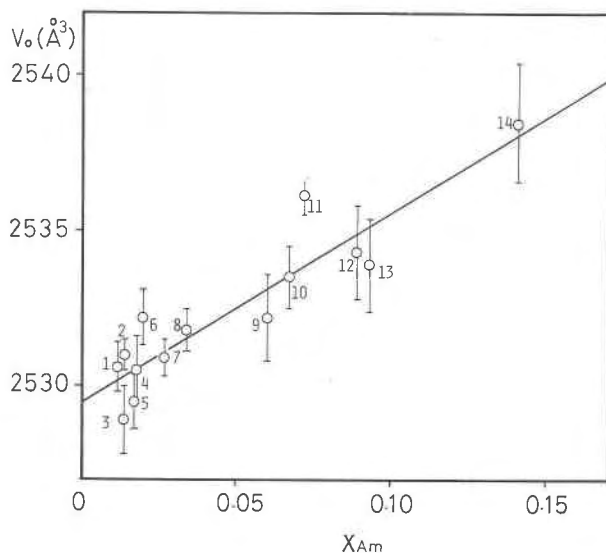


Fig. 1. Unit-cell volume of wairakite as a function of  $X_{Am}$ .

range of the specimens is too limited to clarify entirely the nature of the wairakite–analcime solid solution series. This significant difference between the two values of cell volume, however, indicates that the excess volume of mixing is positive in the calcium-rich part of the series. When the variation of the lattice constants of wairakite is examined in specimens with similar chemical composition, for instance Nos. 3, 4, 5, and 6 and Nos. 10, 12, and 11, it is obvious that a smaller cell volume is associated with larger deviation from cubic symmetry as shown by the values of  $a - b$ ,  $a - c$ , and  $\beta$  in Table 2. This probably indicates the importance of Si/Al ordering in the framework as the controlling factor of lattice constants of wairakite together with the replacement of calcium by sodium ion. Further study on the estimation of the degree and the nature of the contribution from these two factors is needed, for instance, by the examination of specimens artificially prepared by ion exchange from natural wairakites with different states of Si/Al ordering.

It is quite natural that the more ordered distribution of Al in the framework is preferred in calcium-rich specimens in order to minimize the electrostatic energy. This phenomenon is typically observed in the plagioclase series. On the other hand, the mode of substitution in wairakite is of the type  $\text{Ca} \rightleftharpoons 2\text{Na}$  rather than of the plagioclase type  $\text{CaAl} \rightleftharpoons \text{NaSi}$ . Such a difference can probably be related to the looser structural restriction for local charge balance in the wairakite–analcime series.

The relation between the lattice constants and chemical composition can be used for indirect deter-

mination of the sodium content in wairakite, based upon the magnitudes and the modes of variation of the lattice constants associated with the increase of the number of sodium atoms in a unit cell. A regression equation for such purpose is as follows:

$$\text{Na} = -15.8748(a - c) - 16.4222(a - b) - 3.3825\beta + 310.0658 \pm 0.2495$$

Because the crystal lattice of wairakite is pseudo-cubic, the values of  $4 \times d_{400}$ ,  $4 \times d_{040}$  and  $4 \times d_{004}$  are rather good substitutes for the lattice parameters of  $a$ ,  $b$ , and  $c$  and the difference of the value of  $\beta$  can be safely ignored. A simpler equation can be derived, incorporating the values of  $2\theta^{400}$ ,  $2\theta^{040}$ , and  $2\theta^{004}$  for  $\text{CuK}\alpha_1$  radiation:

$$\text{Na} = -10.833(2\theta^{004} - 2\theta^{400}) - 8.933(2\theta^{040} - 2\theta^{400}) + 4.640 \pm 0.2832$$

The simplified equation is as effective for the prediction of the sodium content as the first, although the accuracy of the estimate is somewhat reduced.

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