

Crystal Structure of Joaquinite

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Abstract

The crystal structure of monoclinic joaquinite, ideal formula $\text{NaFe}^{2+}\text{Ba}_2\text{RE}_2\text{Ti}_2\text{Si}_8\text{O}_{26}\text{OH}\cdot\text{H}_2\text{O}$, has been determined by the Patterson method from 2630 diffractometer data, and refined by least-squares to a weighted R of 0.075. The space group is $C2$, and cell parameters are $a = 10.516 \pm 0.003 \text{ \AA}$, $b = 9.686 \pm 0.003 \text{ \AA}$, $c = 11.833 \pm 0.004 \text{ \AA}$, and $\beta = 109.67 \pm 0.003^\circ$, with $Z = 2$. The new independent determination largely confirms a previous one by Cannillo, Mazzi, and Rossi (1972), but there are important differences, including the space group and several additional atoms found in the present study (Na, OH, H_2O). The principal structural unit is a four-membered Si_4O_{12} silicate ring, equivalents of which are linked by TiO_6 octahedra to form sheets parallel to (001). Sheets are stacked facing alternately up and down in the c direction; Ba atoms and water molecules occur midway between sheets on one level, and Na, Fe, and RE atoms on the alternate levels. The Ti octahedra are somewhat out of the plane of the sheets on the Ba- H_2O side, and they share an edge with each other to link sheets in the c direction. The Fe and Na polyhedra, which also link sheets, are very irregular; Fe is 5-coordinated, and Na is 6-coordinated. The orthorhombic form of joaquinite is evidently related to the monoclinic form by a type of unit-cell twinning on an (001) pseudo-mirror plane through Ba and H_2O . Macroscopic twinning of the monoclinic form on this plane and disordered stacking of monoclinic and orthorhombic forms also occur.

Introduction

Joaquinite occurs as small (~ 1 mm) honey-brown crystals associated with benitoite, neptunite, and natrolite in San Benito County, California (Louderbach and Blasdale, 1909; Palache and Foshag, 1932), and also in Quebec (Bell, 1963) and South Greenland (Semenov *et al*, 1967). Satisfactory analyses have been obtained only recently, as the presence of rare-earth elements (RE) and strontium had not been recognized earlier. The composition of material from California and Greenland is somewhat different; Semenov *et al* (1967) suggested the formula $\text{NaBa}_2\text{Fe}^{2+}\text{Ce}_2\text{Ti}_2\text{Si}_8\text{O}_{26}\text{OH}$ for joaquinite from Greenland, and Laird and Albee (1972) suggested the formula $\text{Ba}_{8.1}(\text{Sr}_{1.7}\text{RE}_{6.5}\text{Th}_{0.1})_{8.3}(\text{Ca}_{0.2}\text{Na}_{3.3}\text{Fe}_{3.1}\text{Li}_{0.8}\text{Mg}_{0.1})_{7.5}\text{Ti}_{8.1}\text{Si}_{32.0}\text{O}_{98.7}(\text{OH})_{13.3}$ for material from California. However, the formulas are very similar in the ratios of the cations.

The existence of monoclinic as well as orthorhombic crystals of joaquinite has also been noted only recently (Laird and Albee, 1972; Cannillo, Mazzi, and Rossi, 1972). No chemical differences were detected between the two modifications, which occur

intimately intergrown in the material from San Benito County. The 1 mm sized crystals show orthorhombic external morphology (Palache and Foshag, 1932), but X-ray studies by Laird and Albee (1972) and Cannillo *et al* (1972) have disclosed that these usually consist of finely twinned or disordered monoclinic joaquinite intermixed sometimes with orthorhombic joaquinite, the whole simulating orthorhombic symmetry.

A recent structural study of monoclinic joaquinite by Cannillo *et al* (1972) was unfortunately overlooked until the present study was entirely completed. Most of the important aspects of the structure proposed by them have been confirmed in the present study; however, it seems that they were unable to resolve all the atoms, largely due to the fact that they were forced to use intensity data from precession photographs of a twinned crystal. They also assumed that the space group was $C2/m$, instead of $C2$, as found in this study. A lower residual, more reasonable bond lengths, and better agreement with formulas proposed on the basis of microprobe data demonstrate that the present determination is a significant improvement over that of Cannillo, Mazzi,

and Rossi. The improvement is a consequence of the availability of superior material. Since the present determination was completely independent of the earlier one, it will be largely described as such, with comments when there are important differences in procedure or results.

Experimental

The material used in this study, a typical specimen from San Benito County, consisted of equant crystals with intermixed orthorhombic and twinned monoclinic forms. From several crushed pseudomorphs, only one crystal could be found which was suitable for structure analysis; this crystal had dimensions $0.1 \times 0.1 \times 0.03$ mm and proved to be monoclinic, flattened parallel to (001). Many other crystals examined under the microscope showed obvious twinning and several promising crystals mounted on the precession camera showed admixture of orthorhombic and twinned monoclinic forms as described by Laird and Albee (1972), as well as occasional diffuse reflections as described by Cannillo *et al* (1972). Precession photographs of the crystal selected showed extinctions consistent with space groups $C2$, Cm , or $C2/m$. Cell parameters determined by least-squares refinement of 20 reflections measured on the Picker diffractometer are $a = 10.516 \pm 0.003$ Å, $b = 9.686 \pm 0.003$ Å, $c = 11.833 \pm 0.004$ Å, and $\beta = 109.67 \pm 0.03^\circ$. The chemical composition was assumed to be the same as the average analysis of Laird and Albee (1972), and to conform to the formula they gave (above).

The crystal was mounted on a Picker FACS-1 diffractometer with the a^* axis approximately parallel to the ϕ axis of the instrument. Intensities for 2630 independent reflections were collected in a quadrant of reciprocal space, to a maximum $\sin \theta/\lambda$ value of 0.80. The data were corrected for background and Lorentz and polarization factors using the program ACACA, written by C. T. Prewitt. Of the 2630 reflections, 2244 had intensities greater than four times the background and were accepted for least-squares refinement. Absorption corrections were also made with ACACA, using a Gaussian quadrature subroutine written by G. E. Harlow, Princeton University; the method for this subroutine was suggested by Burnham (1966). The linear absorption coefficient is 98.6 cm^{-1} and transmission factors ranged from 0.43 to 0.75. The programs RFINE II and BADTEA, by L. W. Finger, Geophysical Laboratory, were used to calculate structure factors, for least-squares refinement, and to calculate bond distances and angles and

associated errors. For least-squares refinement, the structure factors were weighted according to the reciprocal of the variance. Atomic scattering factors were taken from Cromer and Waber (1965), with anomalous dispersion corrections from the *International Tables for X-ray Crystallography*. The program system CRYM, most recently modified by G. N. Reeke, Rockefeller University, was used for Fourier syntheses.

Determination of the Structure

The three strongest peaks in the three-dimensional Patterson synthesis, at $x = 0.42, y = 0.25, z = 0.45$; $x = 0.48, y = 0.0, z = 0.005$; and $x = 0.34, y = 0.0$ and $z = 0.90$, were assigned to the Ba-RE cross vector, the Ba-Ba vector, and the RE-RE vector, respectively. These interatomic vectors are almost consistent with the space group $C2/m$; however, the Ba-Ba vector falls slightly, but very distinctly, off the line $x = 0.5, z = 0$. In principle, this is sufficient to determine the space group as $C2$, rather than Cm or $C2/m$, which was assumed by Cannillo *et al* (1972). In addition, a relatively high concentration of Patterson maxima was observed on the Harker plane $y = 0$, with no significant peaks exactly on the Harker line $x = 0, z = 0$. The space group $C2$ was therefore adopted for structure determination; the results proved this assumption to have been justified.

After location of the Ba and RE atoms, completion of the structure proceeded (slowly) by means of repeated difference Fourier syntheses, supplemented in the later stages by least-squares refinement. Atomic positional parameters and isotropic temperature factors are listed in Table 1.

Cations were assigned to sites on the basis of bond lengths (Table 2) and charge balance as well as electron density. The Fe and Na sites must both have considerable substitution of other cations, and one or both are apparently not fully occupied, judging from the analyses (Laird and Albee, 1972). Occupancies, as Fe *vs* Na, were refined for these two sites; other occupancies were not refined, the population of the RE site being assumed to be the same as in the analyses of Laird and Albee (1972).

All oxygen atoms except those designated as OH and H_2O receive Pauling electrostatic bond strengths which total reasonably close to 2.0. The atom designated OH is bonded only to one Fe and two RE atoms. The atom designated H_2O could only be bonded to two Ba atoms, and these are at relatively long distances (3.13 Å).

In the final least-squares refinement, all cations

TABLE 1. Atomic Coordinates and Isotropic Thermal Parameters for Monoclinic Joaquinite*

Atom	x	y	z	**B, \AA^2
Ba	0.2366(1)	0.0	0.0058(1)	0.94(2)
RE	0.1667(1)	0.7467(1)	0.4518(1)	1.17(2)
Ti	0.0490(3)	0.7369(5)	0.1276(3)	0.36(4)
+,++Fe	0.0	0.3694(6)	0.5	0.6(1)
+,++Na	0.0	0.054(3)	0.5	5.9(8)
Si1	0.3773(5)	0.7343(7)	0.2426(4)	0.66(8)
Si2	0.3085(5)	0.2674(7)	0.2432(5)	0.91(9)
Si3	0.1206(6)	0.0375(7)	0.2917(5)	0.80(9)
Si4	0.0929(6)	0.4365(6)	0.2709(6)	0.68(9)
++01	0.0	0.867(2)	0.0	0.6(3)
++02	0.0	0.606(2)	0.0	0.8(3)
03	0.116(2)	0.881(2)	0.251(1)	1.2(2)
04	0.188(1)	0.385(2)	0.191(1)	0.9(2)
05	0.226(2)	0.115(2)	0.237(1)	1.3(3)
06	0.233(1)	0.715(1)	0.133(1)	0.7(2)
07	0.472(2)	0.605(2)	0.229(2)	1.6(3)
08	0.086(2)	0.604(2)	0.268(1)	1.0(2)
09	0.371(1)	0.737(2)	0.375(1)	1.0(2)
010	0.412(1)	0.303(2)	0.372(1)	1.5(3)
011	0.144(2)	0.368(2)	0.403(1)	1.4(3)
012	0.173(2)	0.044(2)	0.443(1)	1.7(3)
013	0.367(1)	0.254(2)	0.133(1)	0.8(2)
014	0.439(2)	0.880(2)	0.203(2)	1.7(3)
++OH	0.0	0.576(4)	0.5	5.0(9)
++H ₂ O	0.0	0.199(3)	0.0	2.6(5)

* Standard errors, in terms of last-quoted significant figure, are given in parentheses.
 **Values of B for cations are equivalent isotropic values, calculated from thermal ellipsoids; full anisotropic data are given in Table 3.
 † Refined occupancy for the Fe site is 0.79 Fe, 0.21 Na, and that for the Na site is 0.75 Na, 0.25 Fe; other sites are assumed to be fully occupied.
 ‡ Atoms O1, O2, and H₂O are in 2_a, and atoms Fe, Na, and OH are in 2_b; all others are in the general position 4_c of space group C₂.

were given anisotropic temperature factors, whereas oxygen atoms were kept isotropic. Table 1 gives equivalent isotropic temperature factors for the cations; full anisotropic data are given in Table 3. When convergence had been obtained (parameter change/error less than 0.1), the enantiomorph was refined. This resulted in a reduction of the weighted *R* from 7.55 to 7.47 percent; thus the hypothesis that the initial configuration is the more correct one can be rejected at better than the 0.05 percent significance level (Hamilton, 1964). It is the second enantiomorph for which the parameters are given in Table 1. Observed and calculated structure factors are given in Table 4.¹ Changing the absolute configuration caused the frac-

¹ To obtain a copy of Table 4, order Document AM-75-006 from the Business Office, Mineralogical Society of America, 1909 K Street, N. W., Washington, D. C. 20006. Please remit \$1.00 for the microfiche.

tional *y* coordinate of the RE atom to shift by about 0.0031 (about 10 sigma for that atom), and that of the Ba atom to shift by about 0.0014 (about 3 sigma) in the same direction with respect to the rest of the atoms, which remained essentially unchanged relative to each other.

The final unweighted *R* was 8.6 percent and the weighted *R* was 7.5 percent. These values are unsatisfactorily high, and a number of areas in the final difference map show high electron densities. The principal problems seem to be in three areas, the RE atom, the OH atom, and the Na atom. When an isotropic temperature factor was used for the RE atom, three subsidiary positive peaks were observed near it in the difference map, one just below it in the *c* direction, and two centered just above it, but separated from each other along the *b* direction. Lesser complementary negative peaks were also observed. These peaks persisted when an anisotropic temperature factor was used, and the apparent thermal ellipsoid was perhaps unrealistically flattened

TABLE 2. Interatomic Distances in Monoclinic Joaquinite*

	Si1	Ti	Ba
06	1.64(1)	01 1.90(1)	01 2.78(1)
07	1.64(2)	02 1.90(2)	02 2.98(1)
09	1.59(1)	03 1.97(2)	04 2.93(1)
014	1.68(2)	06 1.92(1)	05 3.00(2)
		08 2.03(2)	06 3.15(1)
mean	1.64	013 1.95(1)	06 2.74(1)
	Si2	mean 1.94	07 3.07(2)
			013 2.97(2)
04	1.66(2)	Fe	013 2.89(2)
05	1.70(2)		014 2.82(2)
010	1.58(2)	(2)09 2.07(2)	H ₂ O 3.13(2)
013	1.62(1)	(2)011 2.19(2)	mean 2.95
		OH 2.00(4)	
mean	1.64		RE
	Si3	mean 2.10	03 2.60(2)
		Na	08 2.48(2)
03	1.59(2)		09 2.60(1)
05	1.64(2)	(2)09 2.41(3)	010 2.58(2)
07	1.62(2)	(2)010 2.85(3)	010 2.55(2)
012	1.69(2)	(2)012 2.14(6)	011 2.60(1)
mean	1.63	mean 2.47	012 2.61(2)
	Si4		012 2.89(2)
			OH 2.61(3)
04	1.66(2)		mean 2.62
08	1.62(2)		
011	1.61(2)		
014	1.64(2)		
mean	1.63		

*Standard errors, in terms of last-quoted significant figure, are given in parentheses. Distances in angstroms.

TABLE 3. Anisotropic Thermal Parameters and Ellipsoid Data for Cations in Monoclinic Joaquinite*

Atom	Thermal parameters ($\times 10^4$)					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	27(1)	25(1)	13.5(7)	6(1)	2.2(7)	-2.1(8)
RE	20(1)	61(2)	6.2(7)	3(1)	0.4(7)	-8(1)
Ti	12(3)	10(3)	3(2)	0(3)	0(2)	1(2)
Fe	21(5)	16(6)	7(4)	-0-	2(3)	-0-
Na	74(2)	315(52)	73(16)	-0-	44(13)	-0-
Si1	17(4)	18(6)	10(3)	1(4)	1(3)	2(4)
Si2	26(5)	32(7)	10(3)	-7(4)	5(3)	-9(4)
Si3	29(5)	22(6)	7(4)	0(4)	4(4)	0(4)
Si4	26(5)	7(5)	14(4)	0(4)	4(4)	0(4)

Ellipsoid axes							
Rms vib.	Angle to			Rms vib.	Angle to		
	<u>a</u>	<u>b</u>	<u>c</u>		<u>a</u>	<u>b</u>	<u>c</u>
	Ba				Si1		
0.090(3)	101(12)	80(12)	12(8)	0.07(1)	114(71)	116(36)	28(39)
0.100(3)	120(17)	143(18)	98(10)	0.10(1)	69(118)	159(118)	96(67)
0.133(3)	131(9)	66(7)	113(6)	0.10(1)	129(142)	100(64)	120(136)
	RE				Si2		
0.054(4)	94(3)	80(2)	19(2)	0.06(2)	91(11)	66(9)	30(11)
0.105(3)	38(3)	82(2)	73(3)	0.11(1)	43(28)	103(17)	69(25)
0.175(2)	99(2)	20(2)	103(1)	0.13(1)	69(44)	23(35)	105(12)
	Ti				Si3		
0.04(1)	95(15)	104(23)	20(18)	0.07(2)	86(11)	88(18)	23(11)
0.07(1)	75(41)	165(41)	96(25)	0.10(1)	89(23)	177(19)	88(19)
0.084(8)	138(49)	100(33)	111(45)	0.12(1)	147(27)	91(19)	104(27)
	Fe				Si4		
0.07(2)	94(19)	90	16(19)	0.006(2)	88(12)	5(21)	87(20)
0.09(2)	90	180	90	0.009(1)	89(25)	87(23)	166(25)
0.11(1)	142(39)	90	108(34)	0.12(1)	141(34)	88(9)	109(34)
	Na						
0.15(2)	131(22)	90	120(22)				
0.22(2)	57(30)	90	166(20)				
0.39(3)	90	0	90				

* Standard errors are given in parentheses in terms of the last-quoted significant figure. Rms (root-mean-square) vibrations are in angstroms and angles are in degrees.

perpendicular to c^* (rms amplitude 0.05 Å on an axis near c^* , vs 0.10 and 0.18 on the other two axes). A split atom model was refined, but the extra peaks were not greatly reduced in intensity. These anomalies might be due to inaccuracies in the absorption corrections and/or the anomalous dispersion corrections, or to undetected admixture of orthorhombic or twinned monoclinic crystals. The large temperature factor for the OH atom (Table 1) could be related to the anomalies described above in the nearby RE atom. Also, this position might not be

fully occupied; a simplistic interpretation of the chemical analysis requires only 0.7 OH to balance the charges. The large temperature factor for the Na atom is almost certainly due to the presumed wide range of substitution in this site. The apparent thermal ellipsoid is elongated in the b direction (rms amplitude 0.39 Å along b , vs 0.22 and 0.15 perpendicular to b). Difference maps sometimes showed a subsidiary positive peak at $x = 0$, $y = 0.19$, $z = 1/2$, which perhaps indicates the position of cations other than Na in this site. The water molecule also has a

somewhat high temperature factor, but this site may also not be fully occupied.

The OH and Na atoms and water molecule are all in special positions with half the multiplicity of most of the other atoms, hence they contribute least of all to the structure factors in general (Fe is also in a special position, but has higher electron density). The assumption of space group $C2/m$ by Cannillo *et al* (1972) meant that the Fourier peaks for all these four atoms in special positions would appear with halved intensity. It is therefore not surprising that they did not detect the Na, OH, and H₂O atoms, and found only half occupancy for the Fe atom. The position they give for Fe is actually close to a weighted average of the positions of the Fe and Na atoms found in this study.

Formula

The idealized formula, based on the structure determination, is $\text{NaFe}^{2+}\text{Ba}_2\text{RE}_2\text{Ti}_2\text{Si}_8\text{O}_{28}\text{OH}\cdot\text{H}_2\text{O}$, with $Z = 2$ for the monoclinic cell. In reality, there must be abundant substitution of various cations for Fe and Na, and substitution of Sr for rare earths. The average analysis of Laird and Albee (1972) gives total cationic charge per formula unit of 52.7, compared to 53 for the ideal formula above. The difference is well within the precision of the electron microprobe analyses, and furthermore it is possible that the OH site is not fully occupied. Absence of OH could well be correlated with vacancies in the Fe site. The above formula is identical to one of those proposed by Semenov *et al* (1967) and very similar to that of Laird and Albee (1972), with the exception of the water molecule in both cases. The structure determination of Cannillo *et al* (1972) failed to detect the Na, OH, and H₂O atoms and thus gave a rather poor agreement with the formulas previously proposed.

Description of the Structure

The main features of the structure are essentially as given by Cannillo *et al* (1972), with the exception of the three undetected atoms. The principal structural unit is an irregular four-membered silicate ring, which is approximately parallel to (001). Symmetry equivalents of this ring are linked by TiO₆ octahedra into sheets parallel to the (001) face (Fig. 1). These sheets are stacked in the c direction with each being related to the ones above and below by the two-fold axes; thus they face each other in pairs. The Ti octahedra are distinctly "below" the plane of the sheets, about one-quarter of the way to the next sheet. They share edges (the O1 and O2 atoms) with the oc-

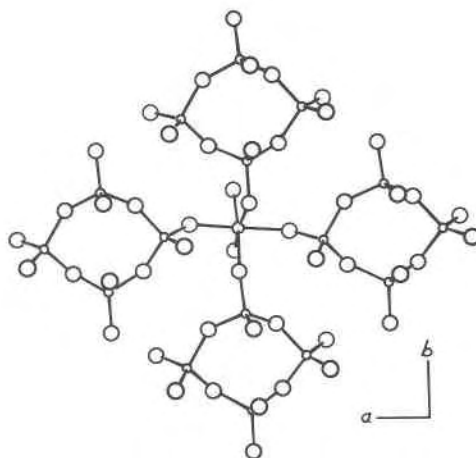


FIG. 1. Perspective view of the sheet structure in joaquinite. Four Si₄O₁₂ rings are joined by each TiO₆ octahedron (center) to form continuous sheets parallel to (001). The silicon atoms are almost in the same plane, but titanium is about 1 Å below the plane. Drawing produced by ORTEP (Johnson, 1970).

tahedra which link the rings in the facing sheet, and one set of two-fold axes passes through these edges. The Ba atoms and water molecules lie in the plane at $z = 0$ between the "bottoms" of the sheets, defining top and bottom on the basis of the location of the Ti atom, as above. This plane is a pseudo-mirror plane, if only the sheets directly above and below are considered (Cannillo *et al*, 1972; their Figs. 4 and 5). The Ba atoms are in irregularly coordinated sites between the rings and the Ti octahedra. The central holes of the rings in successive sheets overlie each other, producing cavities in which the water molecules lie.

The RE, Fe, and Na atoms are sandwiched between sheets which face each other top to top. The Re atoms almost directly overlie the Ti atoms, being slightly below the bisecting plane at $z = 1/2$. Thus they fit into holes left by the Ti octahedra in their downward displacement. The Fe and Na atoms lie exactly in the bisecting plane on a two-fold axis.

The coordination number of both the Ba and RE atoms is high, and although their polyhedra can only be described as irregular, there seem to be no distinct anomalies in bond lengths (Table 1), except that the mean bond length for RE is larger than expected from ionic radii. Evidently the sheet structure as described above can sandwich the Ba and RE cations fairly neatly in a double-decker arrangement. Most of the structural misfit seems to be centered around the Fe and Na sites (Fig. 2), which, located as they are on a two-fold axis, must be considered to be highly constrained by the way in which the sheets fit together. Fe is in an unusual five-coordination with OH at the

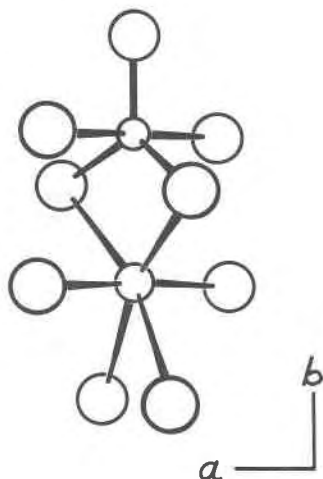


FIG. 2. Perspective view of the Fe and Na coordination in joaquinite. The Fe atom, above, is five-coordinated, with OH at the upper apex. Na is six-coordinated. A two-fold rotation axis runs vertically through the OH, Fe, and Na atoms.

apex, and although the Na site is six-coordinated, the bond lengths are disparate (Table 2).

Polymorphism of Joaquinite

The pseudo-mirror plane at $z = 0$ results in frequent twinning of monoclinic joaquinite, as shown by Cannillo *et al* (1972, their Fig. 5). In a topological sense, the twins can be regarded as stacking faults. If we consider the structural units to be a pair of sheets facing each other across this pseudo-mirror plane, then the "normal" monoclinic structure is composed of these units stacked in the c^* direction with successive displacements of $+3/8 a$, whereas a twin has successive displacements of $-3/8 a$. Some structural adjustments also take place, of course, since twins are mirror-images of each other and cannot be strictly related only by translation.

Many specimens of joaquinite show the twinned monoclinic form only, or have diffuse X-ray reflections indicating essentially random stacking in the c^* direction. Cannillo *et al* (1972) apparently concluded that the orthorhombic form of joaquinite did not exist at all. However, some crystals examined by previous workers and in the present study have definite, sharp X-ray reflections indicating an orthorhombic structure, although this form very often seems to be intermixed on a fine scale with the monoclinic form. Given the cell dimensions ($a = 10.48 \text{ \AA}$, $b = 9.66 \text{ \AA}$, $c = 22.26 \text{ \AA}$) and the possible space groups ($Cc2m$, $Ccm2$, or $Ccmm$) reported, this orthorhombic form must consist of a regular alternation of the $+3/8$ and $-3/8$ stacking modifications of

the monoclinic form. Assuming that the structure is essentially the same as that of the monoclinic form except for stacking, the space group must be $Cc2m$, and the relationship of unit cells would be as shown in Figure 3. The derivation of the orthorhombic structure from the monoclinic one is thus a type of unit-cell twinning, somewhat similar to that found in pyroxenes and amphiboles, and treated at length by Ito (1950).

The approximate coordinates of atoms in the orthorhombic form can be derived from those in the monoclinic cell; the general equations are

$$z_o = \frac{1}{2}z_c + \frac{1}{4},$$

$$x_o = \left(\frac{1}{2} - z_c\right) \cos \beta \frac{c_c}{a_o},$$

where the subscript "o" indicates orthorhombic and "c" indicates monoclinic. The y coordinate is unchanged.

The structure of monoclinic joaquinite has pronounced $C2/m$ pseudosymmetry; the only atoms which are in gross violation of this symmetry are Fe, Na, OH, and H_2O , although the deviations of some of the other atoms from their $C2/m$ positions are fairly large. On the basis of the reported composi-

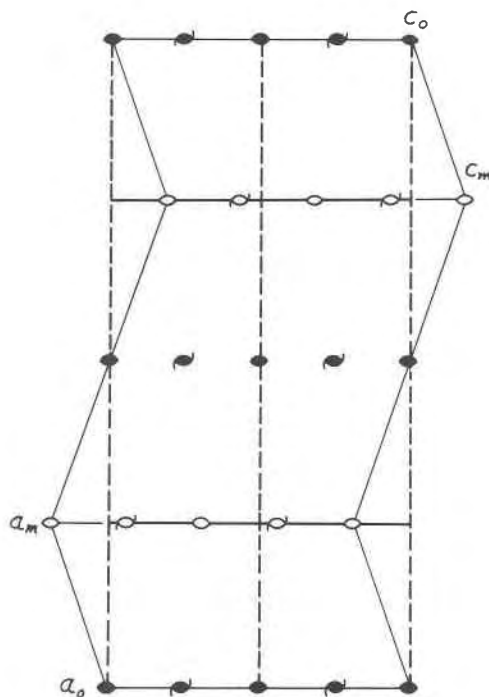


FIG. 3. Probable relationship of unit cells in monoclinic vs orthorhombic joaquinite. Hollow symbols are used for those two-fold rotation and screw axes which are present in the $C2$ monoclinic cell but not in the $Cc2m$ orthorhombic cell.

tions, however, it is very doubtful that there is a structural modification of joaquinite which has true $C2/m$ symmetry, and it is completely impossible for the $C2$ form to transform displacively (with increasing temperature, for example) to $C2/m$; extensive diffusion of the above-named atoms would be required.

Acknowledgment

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