The crystal structures of sjögrenite and pyroaurite

By L. Ingram[1] and H. F. W. Taylor

Department of Chemistry, University of Aberdeen

[Read 8 June 1967]

Summary. Tae crystal structures of sjögrenite and pyroaurite, two stacking modifications of approximate composition $Mg_6Fe_2(OH)_{16}(CO_3).4H_2O$, have been determined by X-ray diffraction using three-dimensional methods. Sjögrenite is hexagonal, with a 3·13, c 15·66 Å, space group $P6_3/mmc$, $Z = \frac{1}{4}$; pyroaurite is rhombohedral, with a_H 3·13, c_H 23·49 Å, space group $R\bar{3}m$ or $R3m$, $Z = \frac{3}{8}$. Both structures are based on brucite-like layers, with magnesium and iron distributed among the octahedral positions. The cations appear to be largely disordered, although ordered regions may occur in some crystals. Between the brucite-like layers are the water molecules and carbonate groups. These are statistically arranged, with their oxygen atoms distributed among a larger number of possible sites.

SJÖGRENITE and pyroaurite are two closely similar minerals that would appear to be stacking modifications of the same basic structure. Frondel (1941) studied them in some detail and reviewed earlier work. Both form platey crystals similar to those of brucite, and have the approximate composition $Mg_6Fe_2(OH)_{16}CO_3.4H_2O$. Chemical analyses, unit cell determinations, and other data indicate that several other minerals are structurally analogous to one or other of them; these include the $Mg^{2+}-Al^{3+}$ minerals, hydrotalcite and manasseïte (Frondel, 1941), the $Mg^{2+}-Cr^{3+}$ minerals, stichtite and barbertonite (Frondel, 1941), the $Ni^{2+}-Fe^{3+}$ mineral, reevesite (White, Henderson, and Mason, 1966), and an unnamed hydroxide mineral containing Mg, Ni, and Fe (Jambor and Boyle, 1964; Lapham, 1965). Brugnatellite ($Mg_6Fe(OH)_{13}CO_3.4H_2O$?; Frondel, 1941) and coalingite ($Mg_{10}Fe_2(OH)_{24}CO_3.2H_2O$; Mumpton, Jaffe, and Thompson, 1965) appear to be somewhat more distantly related, while numerous products have been made artificially that appear

[1] *Née* Hardman.

to belong to the same structural group (Feitknecht, 1940; Glemser and Einerhand, 1950). Like the natural minerals already mentioned, all are essentially hydroxides containing both di- and tri-positive metal cations, both with ionic radii in the region of 0·5–0·8 Å. They have usually been assigned formulae of the type $M^{II}(OH)_2 . \frac{1}{4} M^{III}OOH$, where M^{II} is typically Mg^{2+}, Fe^{2+}, Co^{2+}, or Ni^{2+} and M^{III} is Al^{3+}, Fe^{3+}, Co^{3+}, or Ni^{3+}. The hydroxyl ions can frequently be partly replaced by other anions, in some cases without markedly altering the cell dimensions.

Unit-cell determinations on pyroaurite, sjögrenite, and other natural minerals of the group were reported by Aminoff and Broomé (1930) and Frondel (1941). These showed that pyroaurite was rhombohedral with space group $R3m$, $R32$, or $R\overline{3}m$, and a 3·095, c 23·27 Å, cleavage (0001), all referred to hexagonal axes, and that sjögrenite was hexagonal, with a 3·10, c 15·57 Å, cleavage (0001). Density determinations showed that, in both cases, these unit cells would contain fractional numbers of formula units ($Z = \frac{1}{4}$ for sjögrenite and $\frac{3}{8}$ for pyroaurite); similar results were obtained for the other minerals studied. Both Aminoff and Broomé, and also Frondel, therefore postulated doubled values for a or c or both, although no experimental support for this was obtained. Frondel mentioned as an alternative interpretation the possibility of a statistical structure, defective in CO_3^{2-} content, but considered it unlikely that this was correct.

A different approach to the structure has been followed by the investigators of synthetic preparations. Feitknecht (1940) considered that double hydroxides such as $Co(OH)_2 . \frac{1}{4}CoOOH$ had structures in which ordered and regularly stacked layers of brucite structure were interleaved with amorphous layers of molecular thickness. He showed that $Co(OH)_2 . \frac{1}{4}CoOOH$ had a unit cell analogous to that of pyroaurite. On the hypothesis mentioned above, this would contain three ordered layers of $Co(OH)_2$ separated by amorphous layers of $CoOOH$. Glemser and Einerhand (1950) proposed an analogous structure for $Ni(OH)_2 . \frac{1}{4}NiOOH$. They showed that their model gave qualitative agreement between observed and calculated intensities for fifteen independent X-ray reflections. They assumed that only the ordered part of the structure would contribute to the diffraction effects, and that the interlayer material, being amorphous, could be ignored.

The assumptions implicit in this approach to the structure may be criticized on two grounds. Firstly, it is difficult to understand how a layer approximately 3 Å thick, sandwiched between adjacent layers both of which are ordered, can itself be amorphous; some degree of

order would almost certainly be imposed by the adjacent layers. Secondly, even if it was amorphous, it would contribute in varying degrees to the intensities of all reflections except those with $h.k.\overline{h+k}.0$ indices.

Mumpton, Jaffe, and Thompson (1965) recorded infra-red absorption spectra for sjögrenite and several related minerals. Sjögrenite gave bands in the 3500, 1600, and 1400 cm^{-1} regions, which could be attributed to hydroxyl stretching, water bending, and carbonate stretching vibrations respectively. There were no other definite bands in the region studied (650 to 5000 cm^{-1}).

It was decided to select one or more minerals of the group for structure determination. At the time the present work was carried out, no X-ray structure studies had been reported on any of the minerals other than those already mentioned. After the work had been completed, Allmann and Lohse (1966) reported a structure determination on sjögrenite. In the main, our results agree with theirs, but there are some differences, which will be discussed later.

Experimental

Specimens of sjögrenite, pyroaurite, barbertonite, stichtite, manasseïte, and hydrotalcite were kindly supplied by the British Museum and the U.S. National Museum. All were examined using X-ray single-crystal methods to find which would be the most suitable for a structure determination. All gave reflections showing varying degrees and types of angular spread. Some showed splitting of basal reflections, indicating the existence of regions in parallel orientation, with slightly differing c-axial lengths. Gastuche, Mortland, and Brown (1967) observed a similar effect in synthetic magnesium aluminium hydroxide preparations, which they associated with differences in $Mg^{2+}:Al^{3+}$ ratio. The best specimen was found to be one labelled 'Sjögrenite' from Sweden (B.M. 1926, 1222). It proved to be a mixture of sjögrenite and pyroaurite, which were sometimes found in parallel orientation as described by Aminoff and Broomé (1930) and Frondel (1941). The specimen consisted of lamellar crystals with (0001) cleavage, which were pale brown and almost opaque if more than a few microns thick; ω was found to be 1·567 (in white light), in good agreement with values in the literature. It was not found possible to distinguish the two species optically. Crystals of each of the pure species were selected for structure determinations. Their approximate sizes were: sjögrenite $100 \times 100 \times 5\mu$, pyroaurite, $150 \times 150 \times 2\ \mu$. No thicker crystals could be found that did

not give excessive angular spread of the reflections, and the possibility of considerable absorption errors had therefore to be accepted.

X-ray oscillation, rotation, and Weissenberg photographs about the a-axis were taken of both crystals, using filtered copper radiation. They confirmed the results of Aminoff and Broomé (1930) and Frondel (1941); there were no indications of multiple a- or c-axes, or of splitting of basal reflections. Sjögrenite was found to be hexagonal, with a 3·13, c 15·65 Å. The Laue symmetry was $6/mmm$, and $hh\overline{2h}l$ reflections were absent for l odd. Possible space groups are therefore $P6_3/mmc$, $P\overline{6}2c$, and $P6_3mc$; $P6_322$ is also possible if all atoms are on special positions. If the specific gravity is taken as 2·11 (Frondel, 1941), the atomic contents of the cell given above are $\frac{1}{4}[Mg_6Fe_2(OH)_{16}CO_3.4H_2O]$. Pyroaurite was found to be rhombohedral, with a 3·13, c 23·47 Å, referred to hexagonal axes. The Laue symmetry was $\overline{3}m$, and there were no systematic absences other than those corresponding to the rhombohedral centring; this confirms Frondel's (1941) conclusion that the space group could be $R\overline{3}m$, $R3m$, or $R32$. Assuming the specific gravity to be the same as that of sjögrenite, the atomic contents of this unit cell are $\frac{3}{8}[Mg_6Fe_2(OH)_{16}CO_3.4H_2O]$.

Dr. J. A. Gard kindly examined the sjögrenite specimen by electron microscopy and selected-area electron diffraction. All the crystals observed gave diffraction patterns with hexagonal symmetry. Some showed an a-axis of approximately 3·1 Å, but others had $a = \sqrt{3} \times 3 \cdot 1$ Å. Because of the difficulty in knowing whether a representative sample was being examined, no conclusion could be drawn regarding the relative abundance of the two forms. These results suggest that there may be a tendency to ordering of the metal cations that produces a cell having three times the area on its (0001) face; the larger crystals studied with X-rays could contain both ordered and disordered regions, possibly of differing Mg:Fe ratios. The additional reflections corresponding to the larger cell could not be detected with X-rays, and for the purpose of the structure determination it had to be assumed that the Mg and Fe were statistically distributed, possibly though not necessarily among a single set of positions.

With sjögrenite, the preliminary stages of the structure determination were carried out using intensities estimated visually from multiple-film Weissenberg photographs taken with copper radiation. For the later stages, intensities were obtained from the same crystal, using a Hilger Automatic Linear Diffractometer with filtered molybdenum radiation. The mean of ten background-corrected measurements of the intensity was taken for each reflection. With the lower angle 000l reflections, the results obtained with the automatic linear diffractometer were of doubtful

reliability because of uncertainties in the background correction. The intensities of the 0004 and 0006 reflections were obtained by studying a single crystal with a powder diffractometer. For the very strong 0002 reflection, no satisfactory method was found. Rough estimates of the intensity were used in the initial stages, and were later replaced by calculated values. In the case of pyroaurite, all intensity data (apart from those of the low-angle 000l reflections) were obtained using the automatic linear diffractometer. The same technique was employed as with sjögrenite, except that only eight measurements were made on each reflection.

All computations were made using an Elliott 803 computer, using programmes kindly supplied by Daly, Stephens, and Wheatley (1963) and by North (1964). In addition to the usual Lorentz and polarization corrections, partial absorption corrections were applied as mentioned by Arndt, North, and Phillips (1964). Atomic scattering factor curves were taken from International Tables (1962), with interpolation where necessary, except with hydrogen, for which the data of Stewart, Davidson, and Simpson (1965) were used. The charges on the atoms were assumed to be Mg, $+1$; Fe, $+1.5$; O, -1; C, 0; H, 0.

Structure determination of sjögrenite

Preliminary estimates of the scale and over-all isotropic temperature factors were obtained by assuming that the structure was at least broadly similar to that of brucite and that all atoms therefore lay on $(11\bar{2}0)$ and $(30\bar{3}0)$ planes. A three-dimensional Patterson synthesis gave clear indication of the presence of two brucite-like octahedral layers per cell, with metal cations at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$ and oxygen atoms at $(\frac{1}{3}, \frac{2}{3}, z)$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z)$, and $(\frac{2}{3}, \frac{1}{3}, -z)$, where $z \approx 0.067$ (fig. 1). This is consistent with the centro-symmetric space group $P6_3/mmc$, and it was decided to assume that this applied to the structure as a whole unless contrary evidence appeared.

These results appeared consistent with a structure analogous to that proposed by Glemser and Einerhand (1950) for $Ni(OH)_2 . \frac{1}{4}NiOOH$. It was therefore tentatively assumed that only the Mg was present in the cation sites of the octahedral layers, which would thus contain, on the average, 0.75 Mg per site, one site in four being randomly vacant. A structure factor calculation[1] gave $R = 0.42$, and a subsequent three-dimensional Fourier synthesis gave some indications of possible sites for the iron and remaining oxygen atoms in the interstitial regions between the octahedral layers. Various trial structures based on this hypothesis were investigated, including several with statistical distributions of the iron atoms among what seemed reasonable sites, but all resulted in a worsening of the agreement $(R = 0.43-0.46)$. The possibility was then considered that the magnesium and iron atoms

---

[1] Here and subsequently, R factors were calculated taking the structure factors of unobserved reflections to be one-half those of the weakest observed reflections. The reflections were weighted for multiplicity.

were randomly distributed among the cation sites of the octahedral layers, and structure factors were calculated, for the octahedral layers only, assuming (0·75 Mg+0·25 Fe) per site. The agreement improved markedly (R = 0·33). Fourier and difference syntheses indicated that the remaining oxygen atoms were on or near the positions ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$), i.e., midway between the oxygen atoms of adjacent octahedral
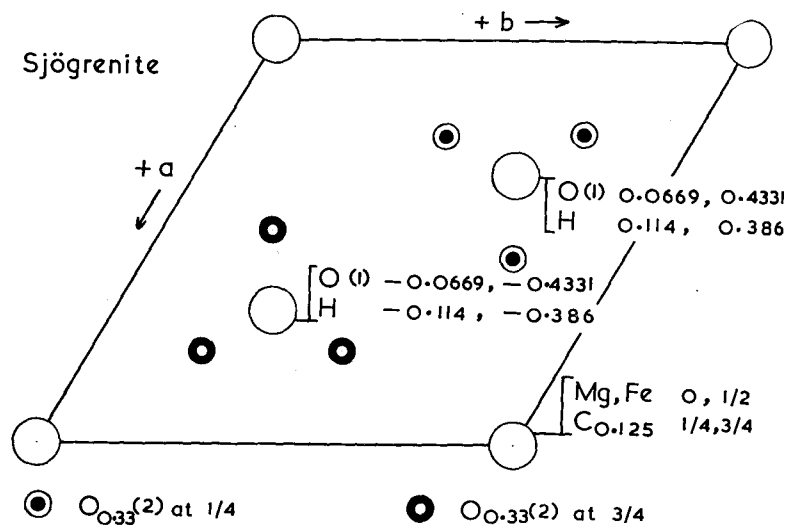

Fig. 1. Sjögrenite: diagram of the structure, as seen in projection along c. Atom designations agree with those in table II, and z-coordinates are given as fractions of c.

layers. These positions will be referred to as the interlayer sites. If it is assumed that the composition is $Mg_6Fe_2(OH)_{16}CO_3.4H_2O$, and that the oxygen atoms of the water molecules and carbonate ions are statistically distributed among the same set of sites, there would be 0·875 oxygen atoms per interlayer site. This value can be approximated to unity without introducing any serious error, especially as chemical analyses (Frondel, 1941) suggest that the content of molecular water is, if anything, somewhat greater than that indicated by the above formula.

A further cycle of refinement using Fourier and difference syntheses suggested that each of the interlayer sites should in reality be split into six equally occupied sites distributed around the three-fold axes and about 0·5 Å away from it, each of which would thus have a statistical occupancy of 0·167 oxygen. It also suggested that the metal cation

should be treated as anisotropic. In this way R was reduced to 0·21. Five cycles of least-squares refinement, using anisotropic temperature factors, reduced R to 0·16 but gave definite indications that each of the interlayer sites was split among only three positions which thus had statistical occupancies of 0·33. These positions are shown in fig. 1. Two

TABLE I. Observed and calculated structure factors for sjögrenite (parameters of Table II)

hk	l	$\lvert F_o \rvert$	F_c	hk	l	$\lvert F_o \rvert$	F_c	hk	l	$\lvert F_o \rvert$	F_c
00	2	—	32·5	20	0	11·0	10·3	11	0	33·9	34·1
	4	34·8	35·1		1	4·7	−3·3		2	27·1	26·4
	6	11·0	−8·3		2	10·6	13·3		4	15·7	16·1
	8	14·8	14·5		3	9·3	−10·6		6	8·8	6·6
	10	4·3	5·4		4	16·1	17·0		8	7·6	7·7
	12	26·3	25·2		5	6·8	−6·3		10	12·3	10·1
	14	19·5	17·4		6	19·1	20·1		12	14·8	14·9
	16	22·0	21·5		7	1·7*	−2·1		14	17·4	15·7
	18	11·5	9·2		8	19·1	18·2		16	17·8	14·8
					9	4·7	4·8				
10	0	8·1	8·3		10	14·9	14·7	21	0	8·9	10·4
	1	13·1	15·8		11	6·8	5·0		1	1·7*	2·1
	2	17·4	17·5		12	8·1	10·2		2	7·6	8·6
	3	16·5	13·5		13	6·3	2·3		3	5·9	6·9
	4	22·9	22·2		14	5·9	8·0		4	12·3	14·1
	5	18·2	18·2						5	4·6	4·5
	6	29·7	29·3	30	0	16·9	16·4		6	13·5	12·9
	7	1·7*	−2·5		1	1·7*	−1·2		7	1·7*	1·5
	8	25·0	23·6		2	14·4	15·4		8	13·5	14·9
	9	1·7*	−3·0		3	1·7*	1·2		9	1·7*	−3·5
	10	23·3	20·4		4	7·6	8·9		10	10·6	10·6
	11	11·4	−10·7		5	1·7*	−1·2		11	3·4	−3·9
	12	13·5	13·4		6	5·9	6·0		12	10·2	9·7
	13	1·7*	−2·8		7	1·7*	1·1				
	14	8·5	10·5		8	4·2	4·1				
	15	1·7*	−1·8		9	1·7*	−1·0				
	16	6·8	7·9		10	7·6	7·3				
	17	4·2	4·9		11	1·7*	0·9	* Assumed value for un-
	18	8·9	9·5		12	11·8	9·2	observed reflection.

further cycles of refinement, based on this last assumption, lowered R to 0·14. Introduction of hydrogen atoms at appropriate sites on the three-fold axes, to complete the hydroxyl groups of the octahedral layers, produced an insignificant decrease in R of from 0·144 to 0·143.

This agreement was considered adequate to show that the structure was probably correct, but all atoms were decidedly anisotropic (e.g., $u_{11} = u_{22} = 0·002$ Å^2, $u_{33} = 0·047$ Å^2 for the metal cations). As the data had been obtained with copper radiation and were uncorrected for absorption, it was suspected that the thermal parameters were incorrect.

At this stage the diffractometer data were obtained. There was reason to believe that these were more accurate, as molybdenum radiation had been used and partial absorption corrections applied. Two cycles of least squares refinement, using the diffractometer data, reduced R to 0·109 and indicated that the metal cation and the oxygen atoms of the hydroxyl groups were almost isotropic, although the interlayer oxygen atoms were not. Fourier and difference syntheses suggested possible
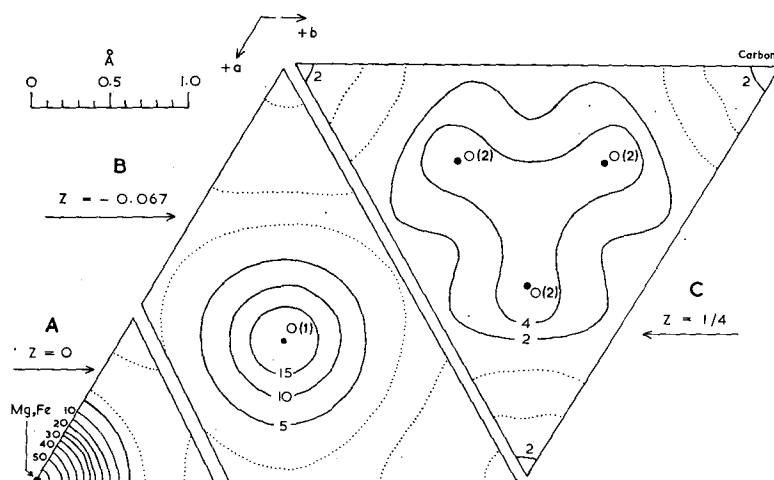

Fig. 2. Sjögrenite: parts of Fourier sections for (a) $z = 0$, (b) $z = -0·067$, (c) $z = \frac{1}{4}$. Atom designations agree with those in table II. The contour interval is 5 eÅ^{-3} in (a) and (b), and 2 eÅ^{-3} in (c); zero contours are dotted.

sites for the carbon atoms, at $(0, 0, \frac{1}{4})$ and $(0, 0, \frac{3}{4})$, with a statistical occupancy of 0·125 atom per site (fig. 1). Three further cycles of least squares refinement lowered R to 0·101. The refinement was stopped at this point; Table I gives observed and calculated structure factors.

Final Fourier and difference syntheses were carried out; the most important sections of the former are shown in fig. 2. The most negative point on the Fourier was $-6·8$ e/Å^3; this was near the metal cation and attributable to ripple. At points well away from the metal cations, the lowest values were around $-0·6$ e/Å^3. The difference Fourier showed electron densities ranging from $-1·3$ to $+1·6$ e/Å^3, with no pronounced features. The integrated electron counts of the peaks were: metal cations, 13·0; oxygen of octahedral layer, 7·2; interlayer oxygen, 2·9 (theoretical values for neutral atoms, 14·0, 8·0, and 2·7 respectively).

Sjögrenite : description of the structure

Table II gives the coordinates and temperature factors of the atoms. The temperature factors are expressed as components of the mean square vibration tensors defined by the expression:

$$f = f_0 \exp -2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^2c^{*2}u_{33} +$$

$$+ 2hka^*b^*u_{12} + 2hla^*c^*u_{13} + 2klb^*c^*u_{23}),$$

where a^*, b^*, c^* are in $Å^{-1}$ and all symbols have their usual meanings.

The metal cations are surrounded by six hydroxyl groups at a distance of $2·09 \pm 0·01$ Å, in a nearly regular octahedron. The sums of the ionic radii, using Goldschmidt's values, are: Mg^{2+}–O^{2-}, $2·10$ Å; Fe^{3+}–O^{2-}, $1·99$ Å, weighted mean, $2·07$ Å. The temperature factors of both metal cations and hydroxyl oxygens are of about the magnitudes normally found in comparable structures. No appreciable significance can be claimed for the positional or thermal parameters of the hydrogen atoms, which must be considered only as plausible values.

The most interesting parts of the structure are the interlayer regions. The section at $z = \frac{1}{4}$ is shown in the Fourier section (fig. 2c) and, over several unit cells, in fig. 3a. Each oxygen site can be occupied by an atom belonging either to a water molecule or to a carbonate group. In each group of three sites, a maximum of one site can be occupied; the chemical analysis shows that in some of the groups (at the most, one in eight, and possibly fewer than this) none are occupied.

For oxygen atoms belonging to water molecules, a system of hydrogen bonding can be postulated if sites in adjacent unit cells are occupied as shown at *ABA* (fig. 3a). The oxygen–oxygen distances between these sites are $2·78 \pm 0·04$ Å; possible approximate positions of hydrogen atoms are shown in fig. 3a. In addition, each oxygen has as neighbours two oxygens of hydroxyl groups (*DD*) at a distance of $2·91 \pm 0·04$ Å, which complete a tetrahedral environment.

In order to form carbonate groups, three oxygen sites in adjacent unit cells must be occupied as shown at *EEE*, and the carbon site between them must be occupied (fig. 3a). The resulting carbonate group lies in the plane of the interlayer oxygen atoms; it has bond angles of $120°$ and bond lengths of $1·27 \pm 0·02$ Å. Only one carbon site in eight is occupied. The Fourier section (fig. 2c) shows a small positive peak corresponding to the carbon sites. No appreciable significance can be claimed for the temperature factors assigned to the carbon atoms.

The temperature factors of the interlayer oxygen atoms (Table II)

TABLE II. Sjögrenite and pyroaurite: atomic coordinates and temperature factors (estimated standard deviations in parentheses)

Sjögrenite	Coordinates (fractions of cell edges)			Temperature factors (Å^2)					
	x	y	z	u_{11}	u_{22}	u_{33}	$2u_{12}$	$2u_{23}$	$2u_{13}$
(Mg, Fe)*	0	0	0	0·004	0·004	0·004	0	0	0
				(0·002)	(0·002)	(0·002)			
O (1)	$\frac{1}{3}$	$\frac{2}{3}$	0·0669	0·012	0·012	0·016	0	0	0
			(0·0004)	(0·004)	(0·004)	0·C04)			
O (2)†	0·235	−0·235	$\frac{1}{4}$	0·052	0·052	0·016	0·084	0	0
	(0·032)	(0·032)		(0·019)	(0·019)	(0·014)	(0·026)		
H	$\frac{1}{3}$	$\frac{2}{3}$	0·114	0·02	0·02	0·02	0	0	0
			(0·008)	(0·08)	(0·08)	(0·08)			
C‡	0	0	$\frac{1}{4}$	0·02	0·02	0·02	0	0	0
				(0·08)	(0·08)	(0·08)			
Pyroaurite§									
(Mg, Fe)*	0	0	0	0·004	0·004	0·004	0	0	0
O (1)	$\frac{2}{3}$	$\frac{1}{3}$	−0·0446	0·012	0·012	0·016	0	0	0
O (2)	$\frac{1}{3}$	$\frac{2}{3}$	0·0446	0·012	0·012	0·016	0	0	0
O (3)†	0·235	−0·235	$\frac{1}{6}$	0·052	0·052	0·016	0·084	0	0
H (1)	$\frac{2}{3}$	$\frac{1}{3}$	−0·0758	0·020	0·020	0·020	0	0	0
H (2)	$\frac{1}{3}$	$\frac{2}{3}$	0·0758	0·020	0·020	0·020	0	0	0

* 0·75 Mg+0·25 Fe.   † 0·33 O.   ‡ 0·125 C   § Space group assumed to be $R3m$.

show distinct anisotropy, which is also apparent from inspection of the Fourier section (fig. 2c).The tensor components in Table II correspond to a vibration ellipsoid having principal axes $u_1 = 0 \cdot 062$ Å^2, $u_2 = 0 \cdot 019$ Å^2, $u_3 = 0 \cdot 016$ Å^2; u_3 is parallel to c and u_1 to the shorter diagonal of the rhomb-based hexagonal cell. The significance of the anisotropy is uncertain. It may represent genuine thermal movement, but other
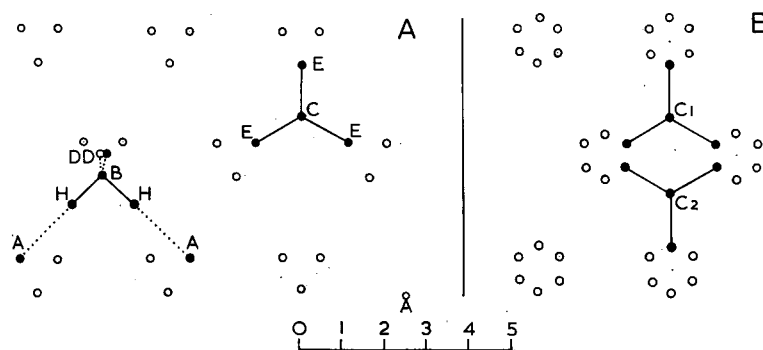

FIG. 3. (a) Sjögrenite: part of the layer at $z = \frac{1}{4}$. The close, triangular groups of circles represent oxygen sites, of which not more than one in each group can be occupied. HBH represents a water molecule, which is hydrogen bonded to oxygen atoms in the same layer at AA and to hydroxyl groups above and below it (shown slightly displaced) at DD. $CEEE$ represents a carbonate group. (b) Pyroaurite: part of the layer at $z = \frac{1}{6}$, assuming the space group of the entire structure to be $R\bar{3}m$. The close hexagonal groups of circles represent oxygen sites, of which not more than one in each group can be occupied. C_1 and C_2 represent two alternative positions for carbon atoms, which cannot coexist in the same layer of the same unit cell. The bonds and oxygen atoms of the corresponding carbonate ions are also shown.

explanations are possible such as slightly differing positions or thermal vibrations depending on whether the oxygen belongs to a carbonate group or a water molecule. It could also arise, in whole or in part, from the fact that the hydrogen atoms of the water molecules were excluded from the structure factor calculations.

Pyroaurite

Because of the less favourable shape of the crystal, the intensity data were expected to be less accurate than those for sjögrenite, and the work was largely restricted to testing a trial structure based on that of the latter. It was assumed that individual octahedral layers were identical with those in sjögrenite and that their stacking was in accordance with the space group $R\bar{3}m$. It was then assumed that the interlayer oxygens

at $z = \frac{1}{6}$ were arranged in the same way as those at $z = \frac{1}{4}$ in sjögrenite; this lowers the symmetry of the entire structure to $R3m$. Fig. 4 shows the resulting structure, and the corresponding parameters are included in table II. A structure factor calculation (table III) based on these assumptions gave $R = 0.137$. This was considered adequate to show
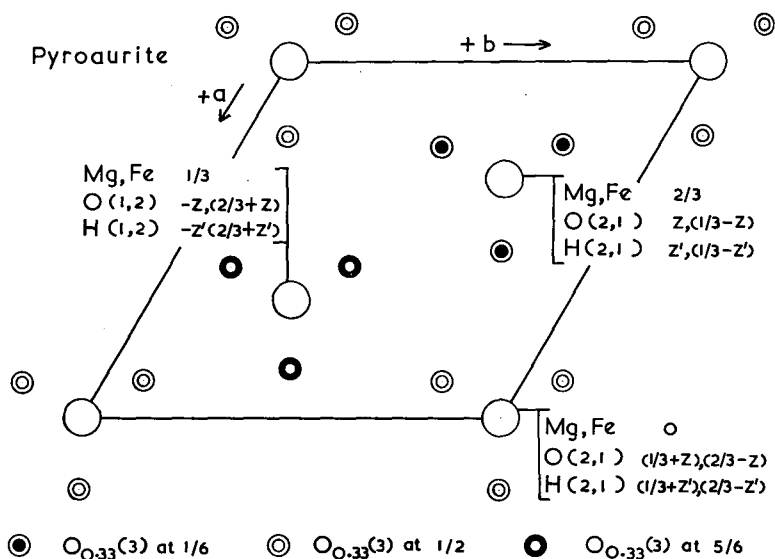

Fig. 4. Pyroaurite: diagram of the structure, as seen in projection along c, assuming the space group $R3m$. Atom designations agree with those in table II, and z-coordinates are given as fractions of c; $z = 0.0446$, $z' = 0.0758$. Carbon atom sites are not shown.

that the structure and mode of stacking of the octahedral layers was correct, and the arrangement of interlayer oxygens at least approximately so.

There is, nevertheless, some uncertainty regarding the interlayer oxygen sites in pyroaurite. In sjögrenite, the evidence favoured the hypothesis that these formed groups of three, rather than of six, disposed around the three-fold axes. It may be presumed that three out of the potential six sites are favoured because of interactions involving the metal cations in the neighbouring octahedral layers, both of which will operate in conjunction in this respect (fig. 1). In pyroaurite, in contrast, the metal cations in the octahedral layers on either side of a given intermediate oxygen layer will operate in opposition to each other

(fig. 4), and there therefore seems no reason whereby one group of three sites disposed around a three-fold axis should be favoured relative to the other. If this argument is correct, the groups of three interlayer oxygen sites become groups of six, and the number of carbon sites is doubled

TABLE III. Observed and calculated structure factors for pyroaurite (space group $R3m$; parameters of Table II)

hk	l	$|F_o|$	$|F_c|$	A_c	B_c	hk	l	$|F_o|$	$|F_c|$	A_c	B_c
00	3	—	50·9	50·9	0	03	0	23·5	23·0	22·9	1·9
	6	52·4	51·0	51·0	0		3	21·4	22·6	22·5	−1·8
	9	16·6	11·2	−11·2	0		6	13·9	12·8	12·7	1·8
	12	22·5	20·8	20·8	0		9	7·0	9·7	9·6	−1·7
	15	5·9	8·8	8·8	0		12	5·4	6·1	5·9	1·6
	18	40·1	37·2	37·2	0		15	7·0	11·2	11·1	−1·4
	21	28·3	26·6	26·6	0		18	12·8	13·1	13·1	1·3
							21	15·5	17·1	17·1	−1·2
01	2	41·2	47·9	47·9	0·7						
	5	57·2	51·1	51·1	−0·6	11	0	50·3	49·4	49·4	0
	8	74·3	65·8	65·8	0·5		3	45·5	39·6	39·6	0
	11	43·3	32·6	32·6	−0·4		6	27·3	23·3	23·3	0
	14	27·3	26·5	26·5	0·4		9	11·2	10·7	10·7	0
	17	5·4	8·1	8·1	−0·3		12	5·4	11·2	11·2	0
	$\bar{1}$	5·4	3·4	−3·4	−0·7		15	9·1	15·6	15·6	0
	$\bar{4}$	7·0	9·5	9·5	0·6		18	20·9	21·7	21·7	0
	$\bar{7}$	7·5	8·1	8·1	−0·6		21	26·8	23·6	23·6	0
	$\overline{10}$	41·2	42·7	42·7	0·5						
	$\overline{13}$	42·3	36·8	36·8	−0·4	12	2	13·9	17·3	17·3	1·1
	$\overline{16}$	46·0	43·1	43·1	0·3		5	25·7	27·9	27·9	−1·1
	$\overline{19}$	25·1	23·7	23·7	−0·2		8	30·5	24·9	24·9	1·0
	$\overline{22}$	13·9	17·7	17·7	0·2		11	26·8	22·3	22·3	−0·9
							14	15·0	11·7	11·7	0·8
02	1	8·0	13·1	13·0	−1·9		17	7·0	9·2	9·2	−0·7
	4	7·0	7·5	7·3	1·8		$\bar{1}$	8·0	12·6	12·6	−1·1
	7	12·3	16·7	16·6	−1·7		$\bar{4}$	5·4	6·0	5·9	1·1
	10	23·0	25·2	25·1	1·5		$\bar{7}$	10·2	13·4	13·4	−1·0
	13	33·2	31·0	31·0	−1·3		$\overline{10}$	18·7	16·9	16·8	0·9
	16	29·4	26·8	26·8	1·2		$\overline{13}$	21·9	23·9	23·9	−0·8
	19	18·7	20·3	20·3	−1·0		$\overline{16}$	23·0	20·3	20·2	0·8
	$\bar{2}$	22·5	25·0	24·9	1·9		$\overline{19}$	18·2	17·4	17·4	−0·7
	$\bar{5}$	38·5	38·2	38·1	−1·8		$\overline{22}$	11·2	9·0	9·0	0·6
	$\bar{8}$	39·1	37·1	37·1	1·7						
	$\overline{11}$	31·0	29·3	29·2	−1·5						
	$\overline{14}$	15·0	16·5	16·4	1·3						

(fig. 3b); the statistical occupancies of both interlayer oxygen and carbon sites are halved, and $R\bar{3}m$ is the space group of the entire structure.

Structure factors were calculated assuming the space group to be $R\bar{3}m$, with each interlayer oxygen site split into six. The R-factor (0·136) did not differ significantly from that found for space group $R3m$.

The differences between the structure factors were seen to lie wholly in their imaginary parts, which are zero for space group $R\bar{3}m$ and lay within the range $\pm$ 1·9 for space group $R3m$ (table III). The differences between structure amplitudes are thus almost negligible and the data are clearly not accurate enough to allow a distinction between the two hypotheses to be made. Three-dimensional Fourier and difference syntheses were carried out based on each hypothesis. They gave inconclusive results for distinguishing between the two hypotheses. Those based on space group $R3m$ were virtually identical in so far as the individual layers were concerned with the corresponding results for sjögrenite (fig. 2a–c).

Discussion

The results show that the structures with statistical distribution of Mg^{2+} and Fe^{3+} on the one hand, and CO_3^{2-} and H_2O on the other, rejected by Frondel (1941) as improbable, are in fact correct, at least as a first approximation, for sjögrenite and pyroaurite. Similar structures probably occur in hydrotalcite, manasseïte, stichtite, barbertonite, reevesite, the un-named nickel-iron hydroxide mineral, and synthetic preparations such as that commonly referred to as $Fe(OH)_2.\frac{1}{4}FeOOH$. It would appear likely that these synthetic preparations also contain sufficient molecular water to bring the ratio of total oxygen to metal cations up to or slightly below 3. Incorporation of other anions presumably occurs, as in sjögrenite and pyroaurite, by displacement of interlayer water molecules or hydroxyl ions.

The present results for sjögrenite agree substantially with those of Allmann and Lohse (1966), the most important difference being that the latter workers found the interlayer oxygen sites to occur principally around the three-fold axes in groups of six, and not of three. This is similar to the result obtained by us for pyroaurite if the space group $R\bar{3}m$ is assumed. Allmann and Lohse considered it possible that the water molecules rotated around the three-fold axes. They were unable positively to locate the carbon sites. The differences between the two proposed structures amount to approximately one electron per interlayer oxygen site, and it would thus be difficult to establish conclusively which structure is correct.

Neither the present results, nor those of Allmann and Lohse (1966) explain why the ratio of dipositive to tripositive metal cations appears to be fixed at 3:1 in most of the natural minerals. Some consideration of packing of the carbonate ions and water molecules in the inter-

mediate layer possibly favours this ratio in cases where the cations are disordered. Where cation ordering occurs, as in the synthetic preparations described by Gastuche, Mortland, and Brown (1967), other ratios are found. This may account for the 6:1 ratio reported for brugnatellite.

References

ALLMANN (R.) and LOHSE (H.-H.), 1966. Neues Jahrb. Min., Monatsh., vol. 6, p. 161.

AMINOFF (G.) and BROOMÉ (B.), 1930. Handl. Kungl. Sven. Vetensk., vol. 9, (3, no. 5), p. 23.

ARNDT (U. W.), NORTH (A. C. T.), and PHILLIPS (D. C.), 1964. Journ. Sci. Instr., vol. 41, p. 421.

DALY (J. T.), STEPHENS (F. S.), and WHEATLEY (P. J.), 1963. Monsanto Research S.A. Final Report No. 52.

FEITKNECHT (W.), 1940. Kolloid-Zeit., vol. 92, p. 257; vol. 93, p. 66.

FRONDEL (C.), 1941. Amer. Min., vol. 26, p. 295.

GASTUCHE (M. C.), MORTLAND (M. M.), and BROWN (G.), 1967. Clay Min., vol. 7, in press.

GLEMSER (O.) and EINERHAND (J.), 1950. Zeits. anorg. Chem., vol. 261, p. 26 and p. 43.

International Tables for X-Ray Crystallography (1962), vol. 3, p. 201. Kynoch Press, Birmingham.

JAMBOR (J. L.) and BOYLE (R. W.), 1964. Canad. Min., vol. 8, p. 116.

LAPHAM (D. M.), 1965. Amer. Min., vol. 50, p. 1708.

MUMPTON (F. A.), JAFFE (H. W.), and THOMPSON (C. S.), 1965. *Ibid.*, p. 1893.

NORTH (A. C. T.), 1964. Journ. Sci. Instr., vol. 41, p. 42.

STEWART (R. F.), DAVIDSON (E. R.), and SIMPSON (W. T.), 1965. Journ. Chem. Phys., vol. 40, p. 3175.

WHITE (J. S.), HENDERSON (E. P.), and MASON (B.), 1966. Proc. I.M.A. Meeting, Cambridge. In preparation.