Acta Cryst. (1956). 9, 773

The Crystal Structure of Ferrocarpholite

By Caroline H. MacGillavry, W. L. Korst*, Elisabeth J. Weichel Moore† and H. J. van der Plas

Laboratorium voor Algemene en Anorganische Chemie der Universiteit van Amsterdam, Netherlands

(*Received* 13 *March* 1956)

Ferrocarpholite, the ferrous iron analogue of carpholite proper, is found to be an 'inosilicate' with $(SiO_3)_n$-chains very similar to those found in the pyroxenes. Its idealized formula is properly written $FeAl_2(OH)_4Si_2O_6$; that of ordinary carpholite is $MnAl_2(OH)_4Si_2O_6$. The classification of carpholite, first given by Strunz, is therefore confirmed.

Introduction

Ferrocarpholite was described as a new mineral by De Roever (1951), who isolated it from rocks collected during the Celebes expedition 1929 of the Netherlands Geological Survey, under the leadership of Prof. H. A. Brouwer. Rotation diagrams of ferrocarpholite and carpholite proper from Wippra showed that the two are isomorphous (De Roever, 1951).

The extremely fibrous character of carpholite, and the length of its fibre period, 5·3 Å, led Strunz (1938) to suppose that carpholite has a chain structure related to that of the pyroxenes, and that its formula should be written $(Mn, Fe)Al_2(OH)_4Si_2O_6$, a classification which has since been accepted in most mineralogy handbooks. The proof, of course, is not conclusive as it stands. Moreover, since the pyroxenes themselves do not contain OH groups it was thought worth while to make a full structure determination.

Properties of the specimen

The chemical composition has been given in De Roever's paper, to which we refer also for morphology, optics, etc. Whereas carpholite has been described by Strunz (1938) as monoclinic, ferrocarpholite is orthorhombic dipyramidal, the crystal class following unambiguously from the space group *Ccca*.

Cell constants were roughly determined from Weissenberg diagrams about the three axes; they were refined from rotation and oscillation diagrams about the *c* and *b* axes in a camera of 5·00 cm. radius, taken with Cu *Kα* radiation, the films being in the asymmetric position.

The cell dimensions thus determined,

$$a = 13{\cdot}77,\ b = 20{\cdot}18,\ c = 5{\cdot}10_9\ \text{Å}\ ,$$

have already been communicated in De Roever's paper; they are believed to be accurate within 0·1%.

All halvings consistent with the space group *Ccca* are strictly observed. From the density, 3·04 g.cm.$^{-3}$, and the result of chemical analysis, De Roever calculated the atomic contents of the unit cell as follows:

	Number of atoms per cell			
Si		16·27		8 × 2·03
Al		14·99	15·81	8 × 1·98
Fe^{III}		0·68		
Ti		0·07		
Mg	1·63	0·07		
		1·56	8·12	8 × 1·01
Mn		0·05		
Fe^{II}		6·51		
H		29·09		8 × 3·64
O		78·92		8 × 9·87

He gives reasons for the supposition that the water content, as determined by loss of weight after prolonged heating, is actually higher than given above; it seems therefore plausible to work with an idealized formula:

$$(F^{II}_{0\cdot8}Mg_{0\cdot2})(Al_{0\cdot95}Fe^{III}_{0\cdot05})_2Si_2O_{10}H_4\ .$$

Determination of the structure

We shall describe our structure determination in some detail, first, because the economical use of Patterson and Fourier methods may be of some interest; secondly, because at one stage some use was made of the minimum-function method (Buerger, 1951), which has not yet been often applied in cases of such complexity, where no heavy atom is present.

As a first step, a projection of the vector map along [001] was calculated. Although it showed some indications of the presence of $(SiO_3)_\infty$ chains of the same type as in the pyroxenes, we were not able to solve the structure from this map. In particular, it proved to be impossible to derive the Fe positions with any certainty; in this compound, Fe is not heavy enough to assign the highest peaks in the Patterson maps to Fe–Fe distances.

Three-dimensional data were then collected from Weissenberg photographs about the *c* axis (0 to 3rd layer), *a* axis (0 to 11th layer) and the zero and first

---

* Present address: Chemistry Department, University of California, Berkeley 4, California, U.S.A.

† Present address: 3 Lincoln Place, Ossining, N.Y., U.S.A.

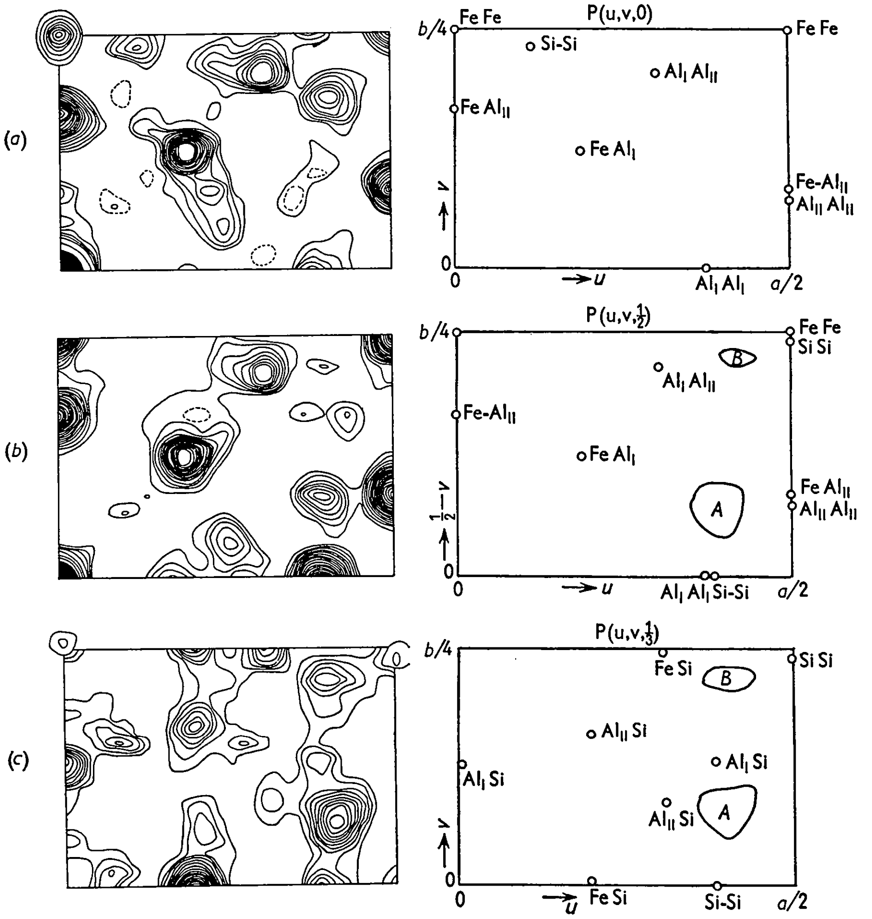

Fig. 1. Patterson sections at (*a*) $w = 0$, (*b*) $w = \frac{1}{2}$, (*c*) $w = \frac{1}{3}$. On the right-hand side the significant interatomic distances are indicated. Overlap of $u, v, 0$ and $u, \frac{1}{2}-v, \frac{1}{2}$ gives the vectors between atoms at $z = 0$ and $z = \frac{1}{2}$; overlap of $u, v, \frac{1}{3}$ and $u, \frac{1}{2}-v, \frac{1}{2}$ identifies vectors between atoms at $z = \frac{1}{6}, \frac{1}{3}, \frac{2}{3}$ and $\frac{5}{6}$. In the regions *A* and *B* there are several Si–O distances overlapping. All the peaks not shown in the right-hand figures can also be interpreted in terms of the structure parameters.

layer about the *b* axis. Notwithstanding the strong secondary radiation, pictures were made with Cu *K* radiation; in order to obtain as much information as possible, some photographs were also made with Mo *K* radiation.

The intensities were estimated visually by two investigators. The data are of rather poor quality, the spots being often split and the background being fairly heavy. The *c*-axis pictures were taken from a crystal ground to a cylinder of 0·6 mm. diameter; the crystal used for the *a*-axis pictures was a platelet with dimensions 0·2 × 0·05 × 0·2 mm. along the three crystallographic axes respectively. In view of other sources of error mentioned above, it was considered that for the latter crystal a correction for absorption would be hardly worth while. As a check, the background of the *a*-axis zero layer line, where irregular absorption might be feared, was measured along five traverses at different θ-values; it has been shown (MacGillavry & Vos, 1943) that in the case of background caused chiefly by fluorescence, the background gives a fairly reliable measure for the transmission factor of the coherently scattered radiation (Bragg spots). As the background for the *a*-axis picture was found to be practically constant, absorption was neglected. For the *c*-axis crystal, the absorption correction for a cylindrical rod was applied.

When the data had been collected and corrected for Lorentz and polarization factors, it became apparent that they showed some peculiar relations not inherent in the space group. Apart from space group absences it was noted that

$hk3$ is absent or very weak for even h and k,
$hk6$ is absent for odd h and k.

On the other hand, reciprocal-lattice planes with $l = 3n \pm 1$ show no indication of pseudo face-centring.

Moreover, it was noted that reflexions $hk5$ show parallelism with the corresponding $hk1$; to a much lesser degree this is the case also for $hk6$ and $hk0$, and $hk4$ and $hk2$ respectively. These peculiarities are explained if we assume that most of the atoms in general position have a z-coordinate near $\frac{1}{3}$, the positions then being:

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0)+$$
$$x, y, \tfrac{1}{3};\ \bar{x}, \bar{y}, \tfrac{1}{3};\ \bar{x}, \tfrac{1}{2}-y, \tfrac{1}{6};\ x, \tfrac{1}{2}-y, \tfrac{5}{6};$$
$$x, \bar{y}, \tfrac{2}{3};\ \bar{x}, y, \tfrac{2}{3};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{5}{6};\ x, \tfrac{1}{2}+y, \tfrac{1}{6}.$$

If *all* the atoms have these z values, it is easily shown that two Patterson sections only, i.e. those at $w = 0$ and $w = \frac{1}{2}$, would contain all the information*. (This cannot be the case, however, since then I_{hkl} would be equal to $I_{h,k,6-l}$, and, as we saw, there is at most a tendency towards this regularity.) Patterson sections were made at $w = 0$, $w = \frac{1}{2}$ and $w = \frac{1}{3}$ (Fig. 1). The last two, which should be brought to coincidence by a shift $0, \frac{1}{2}, \frac{1}{6}$ if all atoms were at $z = \frac{1}{3}$ etc., showed, however, large differences. In fact, the highest peaks in the section $w = \frac{1}{2}$ have no or insufficient coincidences in the plane $w = \frac{1}{3}$. On the other hand, it was found that to these high peaks $u, v, \frac{1}{2}$ there correspond exactly peaks at $u, \frac{1}{2}-v, 0$ (see Fig. 1(*a*) and (*b*)). This points to atoms at $z = 0$, as can be seen from inspection of the vector sets in the space group *Ccca*. A peak $0, \frac{1}{4}, 0$, which had about the expected height compared to the origin peak, was tentatively ascribed to Fe–Fe; Fe^{II} would then be in the position (8*b*): $0, y, 0$, etc., with $y = 45°$. In order to find atoms in the plane $z = \frac{1}{3}$, the minimum function corresponding to this Fe–Fe peak at $0, \frac{1}{4}, 0$, was evaluated in the plane $u, v, \frac{1}{3}$ (Fig. 2). This gave the position of three atoms which, from height, mutual distance and bond directions, could be easily identified as Si and two oxygens attached to it, as indicated in Fig. 2. There are some spurious peaks which could afterwards be interpreted as due to overlap: although the peak $0, \frac{1}{4}, 0$ is single, the minimum function coincides in the plane $u, v, \frac{1}{3}$ with the minimum function corresponding to a Si–Si peak $0, \frac{1}{4}, \frac{2}{3}$.

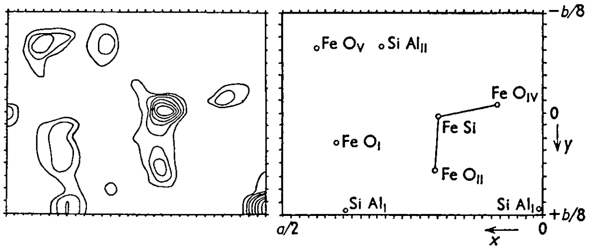

Fig. 2. Minimum function $u, v, \frac{1}{3}$, corresponding to the shift $0, \frac{1}{4}, 0$ (Fe–Fe) and the shift $0, \frac{1}{4}, \frac{2}{3}$ (Si–Si).

Comparison of the sections $u, v, 0$ and $u, v, \frac{1}{2}$ revealed that the strong peaks in these sections could be explained if Al was assumed to be in two special positions, namely Al_{I} in (8*a*) $x, 0, 0$, etc., with $x = 69°$, and Al_{II} in (8*b*) $0, y, \frac{1}{2}$ with $y = 77°$. The rest of the O atoms were then located from chemical considerations, with checks from the Patterson sections. Table 1 lists the rough atomic parameters.

Table 1. *Atomic parameters derived from Patterson sections and minimum function*

	x (°)	y (°)	z (°)
Fe	0	45	0
Al_{I}	69	0	0
Al_{II}	0	77	180
Si	69	47	240
O_{I}	35	20	60
O_{II}	70	20	240
O_{III}	90	60	330
O_{IV}	30	55	240
O_{V}	30	75	60

The peculiarities in intensity distribution, mentioned above, are readily explained on the basis of the positions in Table 1: Fe and both sets of Al have face-centred configurations. Moreover, their contribution to the structure factor is a function of h, k, l (mod. 2). All atoms at $z = \pm\frac{1}{3}$ or $\pm\frac{1}{6}$ do not contribute to *hk*3 and *hk*6 with mixed indices: they have the same geometrical structure factor for *hkl* and $h, k, 6-l$. On the other hand, O_{III}, the only set that does not conform to either of these rules, does not contribute to reflexions with odd l, as it is lying on the glide plane $c(100)_{\frac{1}{4}}$, so that the rule $I_{hkl} = I_{h,k,6-l}$ is strictly valid only where O_{III} atoms do not contribute, that is, for $l = 1$.

Refinement

Structure factors calculated with the positions of Table 1 showed already a remarkably good fit. The structure was refined by two-dimensional Fourier syntheses of the projections along [001] and [100], and subsequently by computing the three-dimensional series:

(*a*) along $x, 0, 0$, for position of Al_{I};
(*b*) along $0, y, 0$, for Fe and Al_{II};
(*c*) in the plane $x, y, \frac{1}{6}$, for Si, O_{I}, O_{II}, O_{IV}, and O_{V};
(*d*) in the plane $x, y, -\frac{1}{12}$, at $x = 84$, 90, and 96°, for O_{III};
(*e*) along $x = 70°$, $y = 46{\cdot}8°$, z, for z value of Si.

The z parameters of the oxygen atoms I, II, IV and V were derived from the electron-density map projected along [100]. Although this projection shows

Table 2. *Final atomic parameters of ferrocarpholite*

	x (°)	y (°)	z (°)
Fe	0	45·0	0
Al_{I}	68·3	0	0
Al_{II}	0	75·8	180
Si	70·0	46·8	237
O_{I}	35·0	20·2	58
O_{II}	74·0	16·9	238
O_{III}	90·0	58·7	328
O_{IV}	29·4	54·3	238
O_{V}	24·7	78·3	58

---

* To avoid confusion, coordinates in vector space are indicated by u, v, w, coordinates in crystal space by x, y, z.

much overlap, it was clear that all these z parameters are closely similar, and close to 60°.

After one cycle, the parameters were as given in Table 2.

As a final check, $hk0$ structure factors were calculated; the corresponding F_o were then scaled and the F_c corrected for temperature factor. The discrepancy factor R was then found to be 0·14, B being taken as 0·45 Å^2. In view of the uncertainties in the experimental intensities (see above) it was not considered worth while to refine the structure further by difference syntheses.

Discussion of the structure

Ferrocarpholite is a silicate of the SiO_3-chain type. In Fig. 3, which shows the structure viewed along the c axis, the part enclosed by broken lines is practically identical with part of the pyroxene structures. In the b direction the SiO_3 chains are linked face to face by zigzag chains of Al in octahedral oxygen surroundings. A novel feature is that the same octahedral arrangement, with chain direction again parallel to the c axis, but with 90° difference in azimuth around this axis, occurs around Al_{II}. In fact, the near surroundings of Al_I and Al_{II} are practically identical. This octahedral stacking is extended on both sides by octahedra around Fe, which follow closely the pattern around Al_{II}. These broader ribbons of octahedra connect the $Si_4Al_2O_{16}$ chains mentioned before.

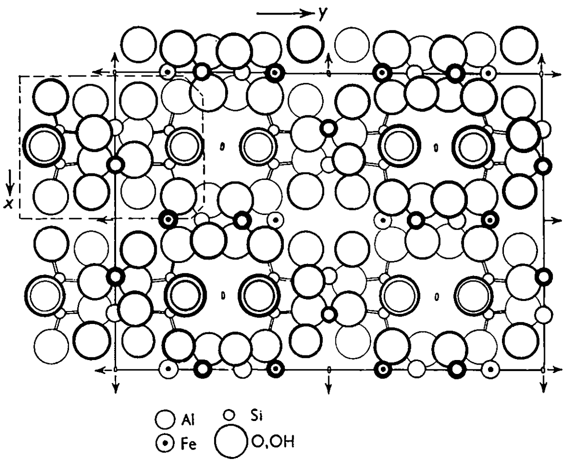

Fig. 3. Structure of ferrocarpholite. The z values range from $-\frac{1}{3}$ (lightest contours) to $\frac{7}{12}$ (heaviest contours).

Electrostatic valencies are practically balanced if it is assumed that O_I and O_V are OH groups.

Interatomic distances are not very accurate, for the reasons mentioned. However, it was found that Fe–O, Si–O and Al–O distances have the expected values: Fe–O = 2·16 Å (average of three, largest deviation from average 0·09 Å); Si–O = 1·64 Å (average of four, largest deviation 0·04 Å); Al_I–O = 1·93 Å, average of three, largest deviation 0·05 Å); Al_{II}–O = 1·92 Å (the average of three, largest deviation 0·07 Å); Si–O_{III}–Si = 132°.

O–O distances within the tetrahedra vary between 2·55 and 2·74 Å, within Al octahedra from 2·50 to 2·96 Å. O–O distances within Fe octahedra, not belonging to Al coordination, vary from 3·16 to 3·24 Å.

Large O–O distances (3·51 Å) occur around the twofold axes parallel to the c axis (Fig. 3) for both O_I–O_I and O_{III}–O_{III}. These atoms do not belong to a common anion polyhedron. As O_{III} carries no hydrogen either, this distance seems to be a pure van der Waals distance, which gives 1·76 Å for the van der Waals radius of oxygen. Since both distances are independent of the z coordinates, they have a high accuracy.

No hydrogen bridges appear to be formed.

We are indebted to Prof. H. A. Brouwer for the loan of a specimen of ferrocarpholite, to Prof. W. P. De Roever for bringing to our attention the structural problem of this mineral, and for his constant interest. The senior author (C. H. McG.) gratefully acknowledges a grant from the Van 't Hoff Fund. Two of us (W. L. K. and E. J. W. M.) have to thank the Fulbright Organization for a fellowship, which made it possible for them to spend a year in the Netherlands. The investigation was carried out with X-ray apparatus put at our disposal by the Organization for Pure Research (Z. W. O.) of the Netherlands. Finally, we wish to thank Mr A. Kreuger for his invaluable technical assistance.

References

Buerger, M. J. (1951). *Acta Cryst.* **4**, 531.
De Roever, W. P. (1951). *Amer. Miner.* **36**, 736.
MacGillavry, C. H. & Vos, H. (1943). *Z. Kristallogr.* **105**, 257.
Strunz, H. (1938). *Z. Kristallogr.* **98**, 60.