

## The crystal structure of phlogopite by neutron diffraction

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**SUMMARY.** The positions of all the atoms including hydrogen have been found by a partial three-dimensional single-crystal neutron-diffraction study in which about one-third of the reflections in the reciprocal sphere to 1.5 Å were measured. The hydroxyl group is perpendicular to the plane of the silicate sheets. The fluorine content of this phlogopite is enough to occupy 25 % of the (OH, F) sites. Site occupancy refinement suggests that there is a small deficiency of hydrogen at the remaining sites and that the two crystallographically different octahedral sites are fully occupied by the same proportions of Mg, Ti, Fe, and Ca.

THE ideal composition of phlogopite mica is  $K_2Mg_6(Si_6Al_2)O_{20}(OH)_4$  but substitutions of ferrous iron for magnesium and of fluorine for hydroxyl are common. Phlogopites containing most hydrogen are most easily altered in ion exchange reactions (Rausell Colom, 1965; Newman, 1969), and this relationship with the hydrogen (or conversely the fluorine) content has been explained as an interaction between the hydrogen of the hydroxyl group and the potassium ion that makes the structure less stable (Bassett, 1960; Newman, 1969). To test this explanation, accurate positions for the hydrogen atoms were sought.

Serratosa and Bradley (1958) showed that thin flakes of phlogopite gave infra-red spectra with no absorbance due to hydroxyl stretching when the beam was perpendicular to the flake, but tilted flakes showed absorbance at  $3710\text{ cm}^{-1}$  that increased with tilt. This suggested that hydroxyl bonds were perpendicular to the cleavage. Muscovite showed a hydroxyl band at  $3620\text{ cm}^{-1}$  that was not changed by tilting the flake. This was interpreted as due to hydroxyl bonds at 15 to 20° to the cleavage plane. This interpretation was confirmed by polarized infra-red measurements on muscovite (Vedder and McDonald, 1963). Biotites show a more complicated pattern of peaks in their spectra, some of which change with tilt and have been interpreted as hydroxyl vibrations influenced by the substitution of Al for Si and of  $Fe^{2+}$ ,  $Fe^{3+}$ , Al, and Ti ions for magnesium at near-by sites (Vedder, 1964).

X-ray diffraction measurements on the same sample of phlogopite used for the neutron diffraction measurements reported here (sample P5 of Newman, 1969) failed to locate the hydrogen atom (see footnote to Table I). But hydrogen atom positions can be found more accurately by neutron diffraction than by X-ray diffraction where the scattering power of hydrogen depends on one electron only. The neutron-scattering length for hydrogen is of about the same magnitude as those for

the other atoms in phlogopite, as shown in the following table (Neutron Diffraction Commission, 1969):

K	Na	Si	Al	Mg	Fe	Ti	Ca	O	F	H
$0.37 \times 10^{-12}$	0.35	0.42	0.35	0.52	0.95	-0.34	0.49	0.577	0.55	-0.372

The negative neutron-scattering lengths for hydrogen and titanium represent a  $0^\circ$  phase change on scattering of neutron waves rather than the usual  $180^\circ$  phase change; as a result the hydrogen atoms appear in Fourier maps as regions of negative nuclear density.

*Experimental.* Neutron-diffracted intensities were measured on a paper-tape-controlled four-circle diffractometer using a monochromated beam of wavelength  $1.17 \text{ \AA}$  and 5 mm diameter and a crystal of phlogopite  $5 \times 5 \times 0.4 \text{ mm}$ , which was cut from a larger sheet using Airbrasive. The neutron-beam intensity is uniform (within 5%; Arndt and Willis, 1966) only over the central 3 to 4 mm diameter that is normally used, but the larger beam diameter used here was necessary to obtain reasonable counting times for such thin flakes of crystal.

Intensity measurements were made over a range of  $6.4^\circ 2\theta$  to allow for some spreading of the spots due to slight splitting of the cut edges of the flake. Intensities were measured in the neutron-beam time available for about a third of the reflections in the sphere out to  $\theta = 45^\circ$ , including *okl*, *hol*, *hhl*, and some *ikl* reflections. No correction was made for absorption as the linear absorption coefficient was calculated to be only  $0.01 \text{ cm}^{-1}$ .

Trial positions for the atoms other than hydrogen were taken from the X-ray study of the same sample. A position for the hydrogen atom was obtained from Fourier and difference nuclear scattering density maps for the *a* and *b* axis projections (three-dimensional Fourier calculations could not be made from the incomplete data). Atomic position, thermal vibration, and scattering length parameters were refined by least squares using all the measured reflections with intensities significantly above the background. The weights for the least-squares calculation were taken from the counting statistics for the individual reflections—some pairs of reflections that by symmetry or by Friedel's law should be equal were more different than would be expected from the counting statistics, suggesting some non-uniformity in the beam or the crystal.

*Results.* The unit cell obtained from X-ray diffraction measurements was confirmed by finding neutron reflections at the angles predicted, but the cell parameters were not further refined by neutron measurements. The cell is *a* 5.322, *b* 9.206, *c* 10.24 Å,  $\beta$  100.03°; space group *C2/m*. Fig. 1 shows the *a*-axis projection of neutron scattering density and positions of the atoms from the least-squares calculations. Negative regions due to termination of series are more severe in neutron than in X-ray Fourier maps, because the scattering length is the same at all angles; but the Fourier maps and difference maps, where termination of series effects are much less, showed no other region of negative density than the one chosen where a hydrogen atom or any large part of one could be placed.

Table I shows the result of a least-squares calculation for 293 observed structure

factors and a model with 61 parameters including 9 site occupancy parameters. The site occupancy in the last column of the table is given as the fraction of the neutron scattering found to that expected from the chemically determined composition  $(K_{1.86}Na_{0.07})(Mg_{5.53}Fe_{0.20}Ti_{0.21}Ca_{0.06})O_{20}(OH_{2.98}F_{1.02})$  (Newman, 1969). The conventional disagreement factor  $R$  for this model is 0.066 and the weighted factor  $WR$  is 0.050. If the site occupancy parameters are not included then  $R = 0.066$  and  $WR = 0.052$  and by Hamilton's (1965) test this would be a highly significantly less good model if most of the error was accounted for by the counting statistics and so was unlikely to be biased.

Table I also contains some results for the X-ray analysis for comparison. The  $R$  factors for the two determinations are 6.6% for neutrons and 6.3% for X-rays, so that the results are of similar accuracy. The difference is in the proportion of the error not due to counting statistics; some of this is not randomly distributed among the observed structure factors and may bias the results. It is estimated from the values of  $\Sigma(w\Delta F)^2/(m-n)$  for the two determinations that for X-rays the total error is about  $2\frac{1}{2}$  times the counting error, but for neutrons about  $5\frac{1}{2}$  times. For this reason Hamilton's test cannot be taken as establishing that a model with site occupancies differing from those based on the chemical analysis and allocated in the conventional way is to be preferred.

Table II shows the bond lengths and angles calculated from the neutron diffraction results.

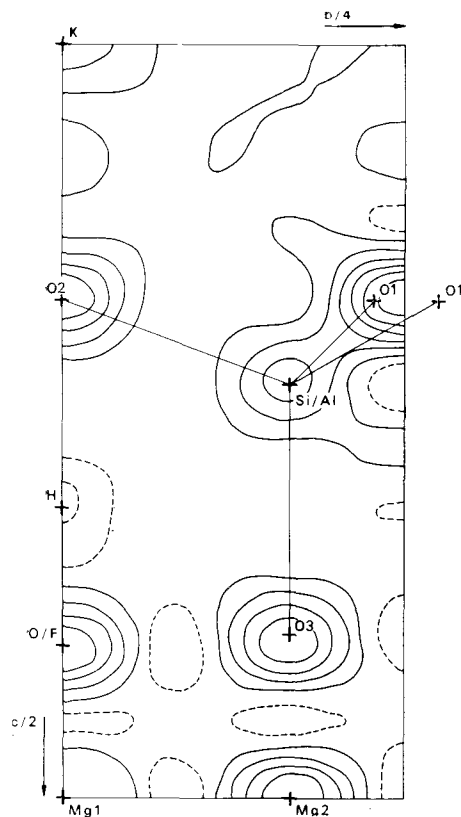


FIG. 1. Neutron-scattering density in  $a$ -axis projection of phlogopite. Fourier synthesis of  $F(\text{obs})$  with phases from final structure including H, arbitrary contour interval, negative contours broken lines.

*Discussion.* Previous attempts to locate the position of the hydrogen atoms in micas were based on infra-red evidence of the direction of the hydroxyl bond. The hydrogen-atom position has now been found directly. In the refinement the thermal motion of the hydrogen atom was taken as ellipsoidal and on this basis the O-H distance is  $0.93 \pm 0.02$  Å. Busing and Levy (1957) found that the neutron diffraction results for the O-H bond length in calcium hydroxide were  $0.936 \pm 0.003$  Å if the motion was treated as ellipsoidal but  $0.984 \pm 0.004$  Å if a more likely 'umbrella' shaped distribution function was used. The direction of the O-H bond should not be much affected by

TABLE I. Atomic parameters for phlogopite from neutron diffraction measurements. Atomic co-ordinates from X-ray diffraction measurements (Rayner, 1974) are given for comparison. Standard deviation on last digit in parenthesis.

Atom site	Co-ordinates			z	Vibration parameters (beta)				Occupancy as fraction of chemical allocation
	x	y			1, 1	2, 2	3, 3	1, 3, 3†	
K	0	0	0	0	0.0194 (6)	0.0041 (27)	0.0068 (14)	0.0018 (21)	0.97 (6)
Si/Al	0.5746 (6) 0.5758 (2)*	0.1664 (7) 0.1667 (1)	0.2267 (4) 0.2273 (1)		0.0034 (12)	0.0018 (9)	0.0020 (4)	0.0015 (4)	0.96 (2)
Mg1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0031 (36)	0.0013 (15)	0.0023 (7)	0.0009 (11)	1.00 (4)
Mg2	0	0.8319 (8) 0.8336 (2)	0.0050 (21) 0.0022 (11)	$\frac{1}{2}$	0.0050 (21)	0.0022 (11)	0.0027 (4)	0.0020 (6)	1.00 (2)
3 O1	0.8279 (6)	0.2281 (5)	0.1693 (3)	0.1693 (3)	0.0116 (10)	0.0077 (8)	0.0028 (3)	0.0025 (3)	1.02 (1)
O2	0.8284 (7) 0.5119 (11)	0.2279 (4)	0.1693 (4) 0.1698 (5)	0.1693 (4)	0.0156 (20)	0.0014 (9)	0.0030 (4)	0.0005 (6)	0.98 (2)
O3	0.5121 (10) 0.6313 (7)	0	0.1691 (5) 0.3918 (3)	0.1691 (5)	0.0065 (13)	0.0039 (7)	0.0024 (3)	0.0017 (4)	1.00 (2)
O/F	0.1309 (13) 0.1330 (8)	0.1674 (5) 0.1669 (4)	0.3915 (3) 0.4001 (5)	0.3915 (3)	0.0050 (24)	0.0036 (10)	0.0025 (6)	0.0015 (7)	0.98 (3)
H	0.0992 (46) 0.18 (6)	0	0.4000 (5) 0.3081 (15) 0.306 (35)†	0.3081 (15)	0.0381 (15)	0.0201 (49)	0.0027 (19)	-0.0010 (23)	0.84 (6)

\* X-ray values are quoted below neutron values.

† For X-rays H at this site refines to a stable position but with an unreasonable temperature factor.

‡  $\beta_{1,2}$  and  $\beta_{2,3}$  are not zero by symmetry for sites  $j$  not on the mirror plane, but the least squares values are not significantly different from zero and the over-all agreement is not significantly improved if they are included.

TABLE II. Bond lengths and angles in phlogopite from neutron diffraction measurements (estimated standard deviation on final digit in parenthesis)

Distances	Angles					
	K-O1	At Mg1	O/F-O3	At Si/Al	O1-O1	
Mg1-O/F	2.952 (6)				83.44°	108.43
O3	2.089 (4)				96.56	108.39
						108.54
Mg2-O/F	2.047 (7)		O3-O3		95.17	110.12
O3	2.066 (7)				84.83	110.57
O3	2.079 (3)					110.73
Mean Mg-O/F	2.050 (5)				81.56	
Mg-O3	2.081 (4)				83.83	
					95.84	90.03
					96.22	90.17
					86.02	
Si/Al-O1	1.662 (6)				95.34	42.62
O1	1.656 (6)				84.98	42.61
O2	1.656 (7)					120.08
O3	1.662 (5)					119.68
Mean Si/Al-O	1.659 (3)					119.6
						119.6

the choice of vibration model. The equal  $119.6^\circ$  angles H–O–Mg (Table II) between the OH direction and the three O–Mg bonds in the octahedral layer show that the O–H bond is perpendicular to the layer, confirming the interpretation of the infra-red evidence for phlogopite. Joswig (1972) has recently reported similar neutron diffraction measurements on a sample of phlogopite and gives an OH distance of  $1.003 \text{ \AA}$ .

The chemical evidence for the proportion of H in the structure is the measured proportion of F, giving  $F_{1.02}H_{2.98}$  equivalent to  $0.74$  H per site. The best neutron result is that  $0.84$  of this expected proportion of H is at the proposed site, but the standard deviation of  $0.06$  makes it uncertain that there is any deficiency, and the site occupancy model is in any case not firmly established. There is some evidence that this sample shows a weaker infra-red OH band intensity than another sample of phlogopite with a similar F content (Newman, private communication), and this may represent a deficiency of H in the structure. The influence of hydrogen ions measured from the pH of the solution used in ion exchange alteration (Newman, 1970) shows that this mica has an unexplained affinity for hydrogen, and this may be due to a deficiency of hydrogen at OH sites in the structure.

Bassett and others suggested that trioctahedral hydroxyl micas exchange potassium more readily than trioctahedral fluor micas or dioctahedral micas because of the proximity of the H of the hydroxyl to the positively charged potassium. The measured distance from H to K in this sample of mainly hydroxy trioctahedral mica is  $3.10 \pm 0.02 \text{ \AA}$ , a close approach for two positively charged atoms, giving a less stable structure than a corresponding fluoro mica.

The mean (Si/Al)–O distance is  $1.659 \text{ \AA}$  and corresponds to a  $26 \%$  occupancy of tetrahedral sites by Al (Smith and Bailey, 1963), agreeing with the  $28 \%$  Al,  $72 \%$  Si derived from the chemical analysis. The average O(apical)–Si/Al–O(basal) angle is  $110.4^\circ$  and O(basal)–Si/Al–O(basal) angle is  $108.3^\circ$  showing that the tetrahedra are somewhat compressed in the plane of the layer.

The bond length, site occupancies by neutrons, and site occupancies by X-rays for the two types of octahedral sites Mg1 and Mg2 are the same and there is such a difference between the scattering power of the Mg, Fe, and Ti atoms for the two radiations that it is very unlikely that there could be an accumulation of one of the three atom types at one of the two sites without causing a detectable difference in one of these parameters.

Although neutron diffraction is a more expensive method of crystal structure analysis than X-ray diffraction it is still of comparable cost (Arndt and Willis, 1966) and might be more widely used to locate hydrogen atoms and in combination with X-ray measurements to study multiply occupied sites. The hydrogen positions in phlogopite are an equal distance from three octahedral ion sites that in most unit cells will be occupied by ions of equal charge, but in muscovite, where one in three of the sites is vacant, the hydroxyl group is about  $70^\circ$  from the vertical position (Vedder and McDonald, 1963; Rothbauer, 1971). Recent accurate neutron diffraction studies have located as little as  $0.08 (\pm 0.01)$  of an atom of hydrogen in buergerite (Tippe and Hamilton, 1971) so it may now be possible to study micas such as biotite by this

method, even if hydrogen atoms occupy a number of sites depending on the pattern of surrounding ions.

*Acknowledgements.* The author wishes to thank the Material Physics Division of A.E.R.E. Harwell for their help in making the neutron diffraction measurements on the Helger-Ferranti diffractometer, on the DIDO nuclear reactor.

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[Manuscript received 18 September 1971; revised 21 March 1974]