

# BIABSORPTION, MÖSSBAUER SPECTRA, AND CHEMICAL INVESTIGATION OF FIVE PHLOGOPITE SAMPLES FROM QUEBEC

D. D. HOGARTH\*, F. F. BROWN† AND A. M. PRITCHARD†

## ABSTRACT

Five samples of phlogopite from intrusive carbonates and vein-dykes of the Gatineau district were studied by means of biabsorption, Mössbauer spectra and chemical analyses. Comparison of optical data and Mössbauer spectra shows that, in samples which exhibit reverse optical absorption, there is a significant amount of ferric iron in tetrahedral sites. The unmistakable Mössbauer absorption at 0.66 mm/sec, which usually appears as a wing on the high-velocity side of the low-velocity peak of high-spin  $\text{Fe}^{2+}$ , provides an easy and reliable method for quantitative estimation of  $\text{Fe}^{3+}_{\text{IV}}$ . Chemical analyses tend to produce somewhat high  $\text{Fe}_2\text{O}_3$  values and in one sample (203) Mössbauer studies suggest some of the ferric iron is present as impurity.

## INTRODUCTION

The difficulties of resolving the valencies of iron and of calculating the structural formulae of phlogopite have long been known. In order to compare three independent methods of determination (Mössbauer effect, optical absorption, and chemical analysis), five phlogopite samples from the Gatineau region of Quebec were selected for detailed examination. These micas were chosen because they were clean (especially lacking in rutile impurities, common in Gatineau phlogopites) and because they were optically homogeneous (with respect to colour and optic angle). For 3 and 391 the material was fine-grained and it was necessary to make mechanical concentrates for Mössbauer and chemical studies. Samples 180, 188, and 203 were comparatively coarse-grained, and splittings were made from a single crystal for each sample. The fine-grained samples (micas 3 and 391) were taken from intrusive carbonates with carbonatite affinities (Hogarth 1966); the coarse-grained samples (micas 180, 188, and 203) were from phlogopite-calcite-pyroxene vein-dykes of the type described by de Schmid (1912) and many later workers.

The samples are low in manganese, and the small quantity of titanium present is thought to have little effect on absorption. Analytical data is presented in Appendix 1. Detailed absorption data for sample 3 has been presented by Faye & Hogarth (1969).

\*University of Ottawa, Ottawa, Canada.

†Physical Chemistry Laboratory, Oxford, England.

## BIABSORPTION

*Theory*

It has been suggested that phlogopite normally owes its absorption to the charge transfer  $O^{2-} \rightarrow Fe^{3+}$  resulting in an intense peak in the near ultraviolet and extending into the visible region (G. H. Faye, personal communication). The absorption is most intense when the electric vector lies in the (001) plane, a plane containing the transition moment for this process. Superimposed on the background (electric vector also in the (001) plane) may be a weak contribution in the red end of the spectrum (peak at about 700  $m\mu$ ) corresponding to the charge transfer  $Fe^{2+}_{VI} \rightarrow Fe^{3+}_{VI}$ , but this will be found only if the specimen contains sufficient total iron and if the  $Fe^{2+}:Fe^{3+}$  ratio is not too high, as in some biotites (Faye 1968). The band(s) associated with the  ${}^5T_{2g} \rightarrow {}^5E_g$  transition of octahedrally coordinated  $Fe^{2+}$  are relatively weak and occur in the near infrared region and consequently play little part in the "biabsorption". The net result of these several factors is an absorption scheme  $A_x < A_{y,z}$  or  $A_x/A_{y,z} < 1$ , where  $A_x$  is the absorbance parallel to  $X$  (optic direction), and  $A_{y,z}$  is the absorbance parallel to  $Y$  or to  $Z$  (optic directions).

For reversely pleochroic phlogopites the absorption scheme becomes  $A_x > A_{y,z}$  or  $A_x/A_{y,z} > 1$ . It was demonstrated by Grum-Grzhimailo & Rimskaya-Korsakova (1964) that phlogopites with a reverse absorption scheme are characteristically low in  $Al_{IV}$  and correspondingly high in  $Fe^{3+}_{IV}$ . Faye & Hogarth (1969) have suggested that the absorption is caused by a charge transfer  $Fe^{3+}_{IV} \rightarrow O^{2-}$  (most effective parallel to  $X$  and producing the continuum) and the  $d-d$  transitions of  $Fe^{3+}_{IV}$  ( ${}^6A_1 \rightarrow {}^4A_1(4G)$ ,  ${}^6A_1 \rightarrow {}^4T_2(4G)$ , and  ${}^6A_1 \rightarrow {}^4T_1(4G)$ ) which have their maximum intensity parallel to  $X$  and impose relatively sharp peaks on the "continuum".

Absorbances cannot be visually resolved in thin sections parallel to 001,  $A_y$  being almost equal to  $A_z$ . However, investigation of thick sheets of phlogopite from more than 250 occurrences in the Gatineau region, Quebec (Hogarth, unpublished) has shown that, although the optic plane ( $XZ$ ) may be either parallel to 010 (meroxene) or perpendicular to 010 (anomite), the absorption scheme with respect to  $Y$  and  $Z$  remains unchanged with the greatest absorption parallel to  $b$  rather than parallel to  $a$ . Because of this, absorption was measured with respect to  $b$  except in thin sections of 3 and 391 where a grain showing maximum biabsorbance was selected from a multitude of randomly oriented grains (giving  $A_x$  and  $A_z$ ).

*Experimental*

Crystals of 180, 188 and 203 were immersed in Araldite and sliced

perpendicular to the cleavage and parallel to  $b$ . The slices were then mounted on glass slides with Canada Balsam and ground to thicknesses of about 0.05 mm. Thin sections of specimens of 3 and 391 were prepared in the conventional manner with thicknesses of about 0.03 mm.

Absorption measurements were made with a Vickers microscope photoelectric cell with S10 cathode, and an interference monochromator. White light was provided with a quartz-iodide lamp and the photoelectric-cell response was directed through a photomultiplier circuit with digital readout. Data is presented in Fig. 1. The measurements were checked on a Leitz microscope using a Wollaston prism and diffraction grating monochromator with biabsorbance calculated according to the double image method recommended by Mandarino (1959). Results of the two methods were in good agreement except in the region 380–420  $m\mu$

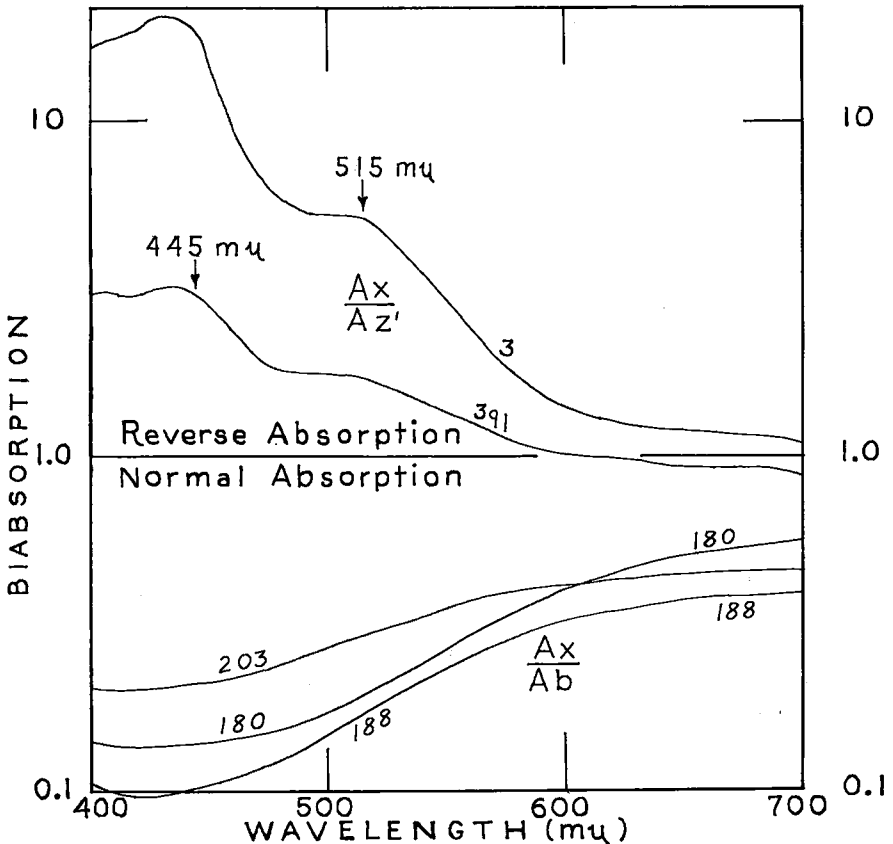


FIG. 1. Biabsorption curves for the five phlogopite specimens.

where the biabsorbance was consistently greater in the direct reading method than in the Wollaston prism method. The discrepancy only became appreciable at wavelengths less than 400 m $\mu$ .

### *Results and discussion*

The biabsorption curves seem to be shaped and positioned mainly by two opposing influences: (i) a charge transfer  $O^{2-} \rightarrow Fe^{3+}_{VI}$  giving a strong background absorbance parallel to  $Z'$  and  $b$ , and (ii) a charge transfer  $Fe^{3+}_{IV} \rightarrow O^{2-}$  strengthened by  $d-d$  transitions of  $Fe^{3+}_{IV}$  which give a strong absorbance parallel to  $X$  (Faye & Hogarth 1969). These effects cannot result in a biabsorption  $Ax/Az'$  less than 1; conversely, the former influence cannot result in a biabsorption  $Ax/Az'$  (or  $Ax/Ab$ ) greater than 1. Since both influences may be operative in the same specimen, the biabsorption curve ( $Ax/Az'$ ) is difficult to interpret quantitatively.

The curves for samples 3 and 391 of the Quebec phlogopites have  $Ax/Az' > 1$ , suggesting mechanism (ii) above, and thus requiring the presence of an appreciable quantity of ferric iron in tetrahedral sites. Furthermore, the inflections of absorption curves at 445 and 515 m $\mu$ , caused by transitions  ${}^6A_1 \rightarrow {}^4A_1E(G)$  and  ${}^6A_1 \rightarrow {}^4T_1(G)$  respectively, suggest more  $Fe^{3+}_{IV}$  in sample 3 than in sample 391.

Conversely samples 180, 188 and 203 have  $Ax/Ab < 1$ . The curves were produced by an appreciable absorption parallel  $b$  and very little absorption parallel  $X$ . The inflections at 445 and 515 m $\mu$  do not appear in these curves and  $Fe^{3+}_{IV}$  seems to be absent or present in very minor quantity in the samples. The fact that these biabsorptions do not decrease near 700 m $\mu$ , shows that the  $Fe^{2+}_{VI} \rightarrow Fe^{3+}_{VI}$  process does not play a significant role, the total amount of iron being too low in the three specimens to produce a detectable effect on the curves.

### MÖSSBAUER EFFECT

The main features of this effect (Mössbauer 1958), which arises from recoilless scattering of gamma-radiation by certain isotopes, are well known. In favourable cases, notably iron-57, through hyperfine interactions, information may be obtained about the electron density at the nucleus, the local electric field gradient (*e.f.g.*), and the magnetic structure of materials. This technique has been shown to give valuable information about the environment and valency of iron-57 in natural and synthetic minerals (Bancroft, Maddock & Burns 1967; Weaver, Wampler & Pecuil 1967).

The areas under the absorption curves, which are Lorentzian, may be

used to give relative site populations when corrected for saturation effects. The area  $A$  beneath a curve may be expressed (Lang 1963) as

$$A = f_s \int_{-\infty}^{\infty} dE [1 - \exp(-\sigma(E) f_a n)]$$

where  $\sigma(E)$  is related to the cross-section at resonance  $\sigma_0$  and the natural linewidth  $\Gamma_0$  by the expression

$$\sigma(E) = \frac{1}{2} \sigma_0 \pi \Gamma_0 K(E) = \frac{1}{2} \sigma_0 \pi \Gamma_0 \sum_{i=1}^q b_i k_i(E)$$

Here  $K(E)$  and the  $k_i(E)$  are normalised for the  $q$  lines in the spectrum, and contain the Lorentzian lineshape function, so that

$$k_i(E) = \frac{1}{4} \Gamma_i^2 [(E - E_{oi})^2 + \frac{1}{2} \Gamma_i^2]^{-1}$$

where the  $\Gamma_i$  are the absorber linewidths. The area beneath the  $i^{\text{th}}$  line is thus

$$A_i = f_s \int_{-\infty}^{\infty} dE [1 - \exp(-t_i k_i(E))]$$

$t_i$  being the effective thickness of the absorber, so that  $t_i = \frac{1}{2} \pi \Gamma_0 \sigma_0 b_i f_a n$ , where  $n$  is the number of Mössbauer nuclei per unit area of the absorber. Since the expansion of the exponential in this expression cannot usually be limited to two terms, it is convenient to write

$$A_i = \frac{1}{2} f_s \pi \Gamma_i L(t_i)$$

where  $L(t_i)$  is a saturation function (Lang 1963). The  $b_i$  represent the proportions of the total absorption under the  $i^{\text{th}}$  line, enabling  $t_i$  to be calculated if the other quantities are known. In the case where lines overlap, the effective thickness will be the sum of the  $t_i$ .

### *Experimental*

The experimental measurements were made in the usual manner using an electromechanical drive system (Cranshaw 1964). The source of cobalt-57 in palladium which decays to give the 14.4 keV Mössbauer gamma-ray was driven at constant acceleration, and the transmitted radiation was detected by a 20th Century PX 130/Xe proportional counter and displayed on a 100-channel pulse height analyser (Harwell type 1524) operating in the time mode. The samples used were either mixed with borax to disperse them if they were in powder form, or were mounted as cleaved sections with the radiation being transmitted perpendicular to the cleavage plane. Spectra were obtained with the absorbers at room temperature and at 77° K, and were calibrated using sodium nitroprusside as a standard absorber, all isomer shifts being quoted relative to the centre of this pattern. The spectra were fitted to

Lorentzian lineshapes on the Oxford University KDF 9 computer using a least squares method.

### Results and discussion

Mössbauer spectra of mica samples 3 and 188 are shown in Figs. 2 and 3 respectively, and the parameters of all the computer-fitted spectra are presented in Table 1. In the figures, the continuous lines represent the individual and overall fits to the experimental points, and in all cases it was possible to achieve a statistically satisfactory analysis using Lorentzian lineshapes. All the spectra showed two main regions of absorption, at about 0.0 and 2.8 mm/sec, giving an isomer shift and quadrupole splitting characteristic of high-spin ferrous iron in an octahedral environment, the sixth *d*-electron giving rise to the *e.f.g.* It has been shown (Ingalls 1964) that any contribution to the *e.f.g.* from lattice charges acts in opposition to this other *e.f.g.*, and the values obtained for the micas suggest that the environment of the  $\text{Fe}^{2+}$  ions is fairly symmetrical. The

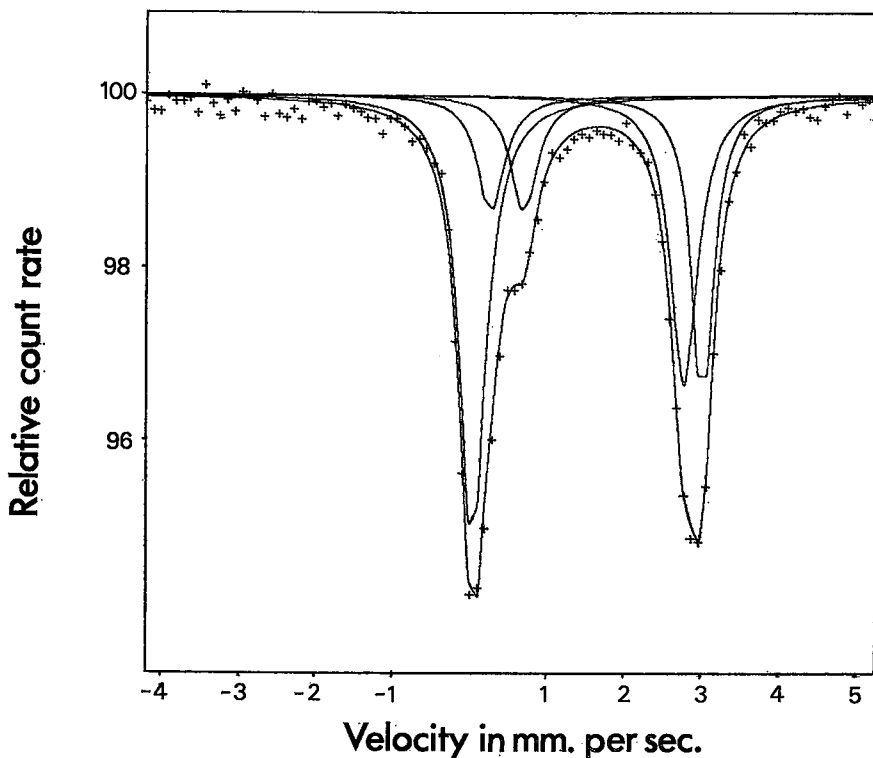


FIG. 2. Mössbauer spectrum of specimen No. 3.

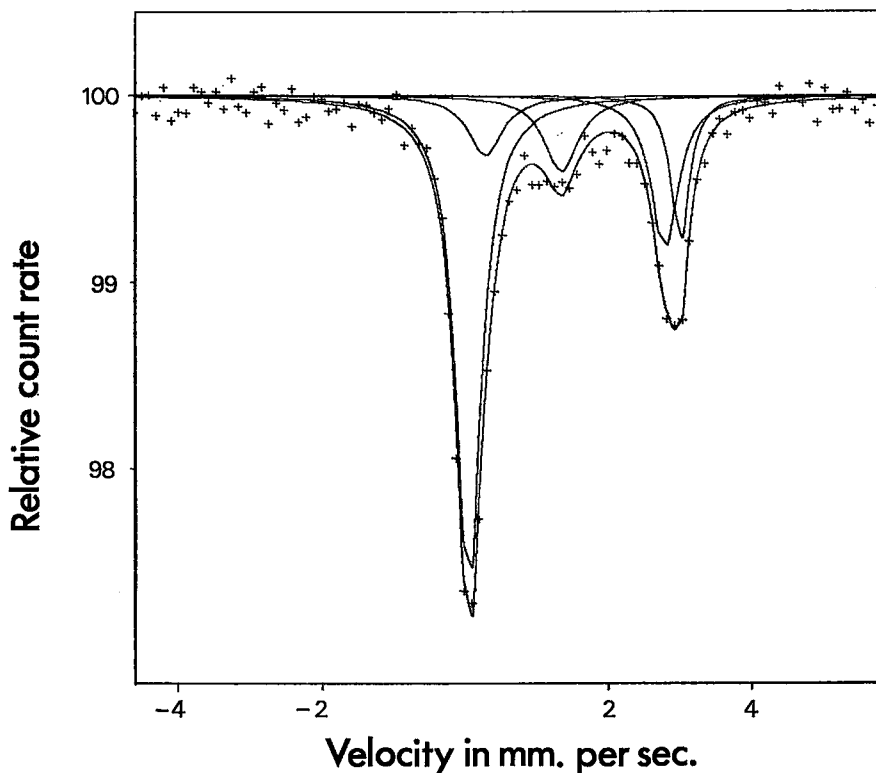


FIG. 3. Mössbauer spectrum of specimen No. 188.

line at lower velocity is Lorentzian within the limits of analysis if due account is taken of the absorptions on the high-velocity wing, but that at higher velocity is best fitted by two Lorentzians arising from the two octahedral sites in the mica structure, the linewidths then being very similar to that of the lower velocity peak, as expected. The failure of other workers (Bowen, Weed & Stevens 1969) to observe this phenomenon may be attributed to their larger observed linewidths. In an isotropically orientated powder with no anisotropy of the recoilless fraction the two lines arising from the quadrupolar interaction should be of the same width and intensity, but any ordering of the principal axes can produce unequal intensities, since the absorption cross-sections for the two transitions vary with the angle  $\theta$  between the incident radiation and the principal axis of the *e.f.g.* (assumed to be axially symmetrical) according to the relation.

$$I_{\pm 3/2 \rightarrow \pm 1/2} / I_{\pm 1/2 \rightarrow \pm 1/2} = (1 + \cos^2 \theta) / (\frac{5}{2} - \cos^2 \theta).$$

TABLE 1. OBSERVED MÖSSBAUER PARAMETERS OF PLEOCHROIC MICAS

(all  $\pm 0.05$  mm/sec)  $\delta$  = isomer shift;  $\Delta E_q$  = quadrupole splitting;  $\Gamma$  = linewidth

Sample	Octahedral Fe <sup>2+</sup>			Octahedral Fe <sup>3+</sup>			Octahedral Fe <sup>3+</sup>			Tetrahedral Fe <sup>2+</sup>		
	$\delta$	$\Delta E_q$	$\Gamma$	$\delta$	$\Delta E_q$	$\Gamma$	$\delta$	$\Delta E_q$	$\Gamma$	$\delta$	$\Delta E_q$	$\Gamma$
3	1.44	2.76	0.34	1.54	2.97	0.34						
391	1.45	2.76	0.36	1.55	2.95	0.36	0.90	1.22	0.36	0.45	0.44	0.35
180	1.43	2.79	0.38	1.54	3.01	0.38	0.80	1.15	0.46	0.47	0.44	0.33
188	1.41	2.76	0.40	1.52	2.97	0.40	0.76	1.06	0.59			
203 <sup>a</sup>	1.40	2.62	0.45	1.50	2.82	0.45	0.79	0.94	0.59			
203 <sup>b</sup>	1.42	2.74	0.43	1.54	2.95	0.43	0.68	0.95	0.48			

<sup>a</sup>Data for absorber at 295° K.<sup>b</sup>Data for absorber at 77° K.



This effect has been found in biotite (Pollak, de Coster & Amelinckx 1962), and in a number of other trioctahedral and dioctahedral micas (Bowen, Weed & Stevens 1969) and is shown by all the micas examined in this study. Our failure to produce equalisation of the intensities by grinding the samples in a mortar indicates that cleavage occurred along the easy plane into smaller platelets; changing the angle of incidence of the sample to the gamma-ray beam which produced the expected change in intensities, supporting the interpretation. Because the lower velocity lines overlap it is not possible to estimate the relative populations of ferrous iron in the two sites, there being no reason to expect that the principal axes of the *e.f.g.*'s will be parallel. Assignment of the two pairs of lines to the sites requires more detailed knowledge of the iron-oxygen distances, and the charges on the oxygens, than is at present available.

The presence of ferric iron is shown by weaker absorptions between 0.2 and 1.5 mm/sec. With the exception of sample 203, these lines may be grouped in two pairs with different isomer shifts and quadrupole splittings, though in only one case (sample 391) are both pairs required to fit the data. The difference in the isomer shifts is too large for both to be attributable to octahedrally-coordinated  $\text{Fe}^{3+}$ , since the data for  $\text{Fe}^{2+}$  in these sites shows them to be very similar. In sample 188 (Fig. 3) only the site with the larger isomer shift and quadrupole splitting is occupied, and the magnitude of the latter quantity, 1.06 mm/sec, strongly suggests that the site is an octahedral one, all values so far reported for tetrahedrally-coordinated ferric iron being significantly lower. In sample 3 (Fig. 2) the ferric absorption has only the lower isomer shift and quadrupole splitting, and is assigned to  $\text{Fe}^{3+}$  in tetrahedral sites. A similar decrease of the isomer shift with coordination number has been found in chloro-complexes of iron (Bancroft, Maddock, Ong & Prince 1966), and arises from a larger covalent interaction in the tetrahedral species which deshields the *s*-electrons of iron, though in iron orthoclase this decrease is small (Brown & Pritchard 1969). The linewidths of the tetrahedral  $\text{Fe}^{3+}$  peaks are narrow by comparison with the octahedral ones, which are more variable and may reflect the presence of  $\text{Fe}^{3+}$  in the two octahedral sites.

The parameters of the Mössbauer spectra are the same within experimental error at 295° K and at 77° K for all the samples except 203, the constancy of the isomer shift indicating that the lattice vibrations are hardly excited at room temperature, and the absence of a variation in the quadrupole splitting showing that the ground state of the iron ions contains little if any mixing of the *d*-wavefunctions. Although the parameters for sample 203 agree well with those of the others at 77° K, the spectrum at 295° K shows a somewhat reduced quadrupole splitting for  $\text{Fe}^{2+}$ ,

and nearly twice the absorption for  $\text{Fe}^{3+}$  which is found at  $77^\circ\text{K}$ . This fact, together with the lower isomer shift recorded at  $77^\circ\text{K}$  for  $\text{Fe}^{3+}$ , may be explained if most of the  $\text{Fe}^{3+}$  ions are present in a different site from those already mentioned, possibly as an impurity. The decrease in the area of the peaks could be explained by the onset of cooperative magnetic interactions at low temperatures, broadening the peaks and making them difficult to distinguish from random variations in the spectrum, and eventually producing a six-line spectrum below  $77^\circ\text{K}$ . For calculations of relative site populations the data obtained at  $295^\circ\text{K}$  were therefore used.

In order to derive relative site populations from the observed areas of the absorptions, an estimate of the effective thickness  $t_i$  must be made. For iron-57,  $t_i = 0.54 w f_a b_i$ , where  $w$  is the weight of iron per square centimetre of the absorber (assuming natural isotopic abundance) and the other quantities have the same significance as before. We did not measure  $f_a$ , but estimate it to be  $0.6 \pm 0.1$  by comparison with the absorption intensity obtained from other iron compounds of known  $f_a$ . Although it is possible that  $f_a$  is different in other sites, the observed areas vary so little with temperature that the difference may be neglected, in agreement with other work (Bowen, Weed & Stevens 1969). The evaluation of the  $b_i$  is less straightforward since the observed linewidth is the sum of the linewidths of source and absorber. The factor 0.54 was calculated assuming that the absorber had the natural linewidth of 0.10 mm/sec so that a correction has to be made for the widths  $\Gamma_i$  of the absorber lines which can reduce  $t_i$  considerably. We find a linewidth of 0.15 mm/sec for our source, so that the calculated  $t_i$  must be multiplied by a factor which varies between 0.55 and 0.23. Assuming that the  $b_i$  are to a first approximation proportional to the intensities of the lines, we find that the largest value of  $t_i$  is 0.4, and thus the smallest value of  $L(t_i)/t_i$  is 0.91. The assumption that the site populations are proportional to the areas of the absorption peaks thus introduces an error of at most 10 per cent. Since the absorption of the  $\text{Fe}^{3+}$  ions only overlaps that from the  $\text{Fe}^{2+}$  ions to a small extent, when most of the iron is present in the ferrous form the calculation of the occupancy of octahedral and tetrahedral sites by  $\text{Fe}^{3+}$  will be subject to a much smaller error on this account, and the major limitation is likely to be the statistical scatter of the experimental data.

## CONCLUSIONS

The results of the Mössbauer calculations, together with the analytical figures for the samples, are set out in Table 2. The Mössbauer measure-

TABLE 2. ANALYSIS OF SITE POPULATIONS

Sample	Fe <sup>2+</sup>		Fe <sup>3+</sup> <sub>VI</sub>		Fe <sup>3+</sup> <sub>IV</sub>		Per cent Total Fe <sup>3+</sup> as Fe <sup>3+</sup> <sub>IV</sub>	
	Anal.*	Möss.	Anal.*	Möss.	Anal.*	Möss.	Anal.*	Möss.
3	0.49	0.57	0	0	0.28	0.20	100	100
391	0.67	0.68	0	0.05	0.12	0.06	100	54
203	0.16	0.53	0.31	0.12**	0.18	0	37	0
180	1.06	1.20	0.17	0.07	0	0	0	0
188	0.16	0.25	0.15	0.06	0	0	0	0

\*Cations per 24 (O + OH + F).

\*\*See text.

ments give only the relative quantities of iron in the various environments, so that no check can be made of the overall iron concentration. However, it is immediately obvious that although, with one glaring exception (203), there is a very general agreement in the amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> present, the analytical technique used overestimates the amount of ferric iron present, and it thus seems likely that some unexpected oxidation is taking place during the analysis. The correlation between the amount of tetrahedral ferric iron and the biabsorbance is qualitatively good, the normally pleochroic micas 180, 188 and 203 being those with the least amount of Fe<sup>3+</sup><sub>IV</sub> and the reverse ones having the most. All three methods suggest more Fe<sup>3+</sup><sub>IV</sub> in sample 3 than 391. The presence of some octahedrally-coordinated ferric iron in sample 391 does not affect the pleochroism, and this gives very strong support to the proposal of Faye & Hogarth (1969) about the nature of the charge-transfer process which gives rise to it.

Of the 3 methods the Mössbauer is probably the most accurate. For the determination of ferric iron in the tetrahedral position, it is reliable provided the concentration is sufficiently high (the lower limit for quantitative evaluation is approximately 3 per cent of the total iron).

#### ACKNOWLEDGMENTS

We thank Chemistry Division A.E.R.E., Harwell, for the loan of the Mössbauer equipment. We also thank the Department of Mineralogy and Petrology of the University of Cambridge for providing facilities for much of the optical absorption work and especially Dr. N. F. M. Henry for many valuable suggestions. Dr. J. A. Maxwell, of the Geological Survey of Canada, kindly determined FeO and Fe<sub>2</sub>O<sub>3</sub> in sample 180. One of us (D.D.H.) gratefully acknowledges a grant from the Geological Survey of Canada (No. 15-63) which defrayed costs of analyses.

## APPENDIX I. PHLOGOPITE FROM OLD CHELSEA REGION, QUEBEC

H. B. Wiik, Helsinki, Analyst  
 Samples 188, 203, 391 and 3  
 H. B. Wiik, and J. A. Maxwell, Analysts  
 Sample 180

	180	188	203	391	3
CaO	0.00	0.00	0.00	0.05	0.20
K <sub>2</sub> O	9.50	10.50	9.96	10.17	9.79
Na <sub>2</sub> O	3.03	2.32	2.40	0.45	0.46
MgO	19.48	25.43	24.34	23.69	26.05
MnO	0.07	0.03	0.06	0.03	0.05
FeO	8.48	1.30	1.30	5.70	4.08
TiO <sub>2</sub>	1.35	1.20	1.10	0.15	0.17
Fe <sub>2</sub> O <sub>3</sub>	1.54	1.39	4.52	1.11	2.66
Al <sub>2</sub> O <sub>3</sub>	13.30	14.42	12.34	10.70	9.97
SiO <sub>2</sub>	38.82	40.02	39.48	42.00	41.37
H <sub>2</sub> O <sup>+</sup>	1.48	1.90	2.45	4.45	4.15
H <sub>2</sub> O <sup>-</sup>	0.55	30	0.45	0.02	0.00
F	3.60	2.70	2.55	2.90	2.15
P <sub>2</sub> O <sub>5</sub>	—	—	—	0.01	—
	101.20	101.51	100.95	101.41	101.10
O = F	1.52	1.14	1.07	1.22	0.91
Total	99.68	100.37	99.88	100.19	100.19
180	Hoist at Forsyth shaft, Ironside	Y = 1.596	Y = b	Y ≈ Z dark brown	X light brown
188	1300 feet north of Pinks Lake	Z = 1.582	Z = b	Y ≈ Z dark brown	X light brown
203	6500 feet northwest of Old Chelsea	Z = 1.584	Z = b	Y ≈ Z dark brown	X light brown
391	McCloskey's field, Gatineau Parkway	Y = 1.582	Y = b	Y ≈ Z dull green	X orange brown
3	McCloskey's field, Gatineau Parkway	Y = 1.582	Y = b	Y ≈ Z pale orange	X orange brown

## REFERENCES

- BANCROFT, G. M., MADDOCK, A. G., ONG, W. K. & PRINCE, R. H. (1966): Spectra of chloroferrate (III) compounds, *J. Chem. Soc. (A)*, 723–725.
- BANCROFT, G. M., MADDOCK, A. G. & BURNS, R. G. (1967): Applications of the Mössbauer effect to silicate mineralogy—I. Iron silicates of known crystal structure, *Geochim. Cosmochim. Acta*, **31**, 2219–2246.
- BOWEN, L. H., WEED, S. B. & STEVENS, J. G. (1969): Mössbauer study of micas and their potassium-depleted products, *Am. Mineral.*, **54**, 72–84.
- BROWN, F. F. & PRITCHARD, A. M. (1969): The Mössbauer spectrum of iron orthoclase, *Earth Planet. Sci. Lett.*, **5**, 259–260.
- CRANSHAW, T. E. (1964): A drive and waveform generator for Mössbauer experiments using a multichannel analyser, *Nucl. Instr. Methods*, **30**, 101–105.
- FAYE, G. H. (1968): The optical absorption spectra of iron in six-coordinate sites in chlorite, biotite, phlogopite, and vivianite. Some aspects of pleochroism in sheet silicates, *Can. Mineral.*, **9**, 403–425.

- FAYE, G. H. & HOGARTH, D. D. (1969): On the origin of "reverse" pleochroism of a phlogopite, *Can. Mineral.*, **10**, 25-34.
- GRUM-GRZHIMALO, S. V. & RIMSKAYA-KORSAKOVA, O. M. (1964): Absorption spectra of phlogopite holding trivalent iron in fourfold coordination, *Dokl. Akad. Nauk S.S.S.R.* (in translation), **156**, 123-125.
- HOGARTH, D. D. (1966): Intrusive carbonate rock near Ottawa, Canada, *Min. Soc. India, I.M.A. Volume*, 45-53.
- INGALLS, R. (1964): Electric-field gradient tensor in ferrous compounds, *Phys. Rev.*, **133**, A787-A795.
- LANG, G. (1963): Interpretation of experimental Mössbauer spectrum areas, *Nucl. Instr. Methods*, **24**, 425-428.
- MANDARINO, J. A. (1959): Absorption and pleochroism: two much-neglected optical properties of crystals, *Am. Mineral.*, **44**, 65-77.
- MÖSSBAUER, R. L. (1958): Kernresonanzfluoreszenz von Gammastrahlung in Ir-191, *Z. Physik*, **151**, 124-143.
- POLLAK, H., DE COSTER, M. & AMELINCKX, S. (1962): Mössbauer effect in biotite, *Phys. Stat. Sol.* **2**, 1653-1659.
- DE SCHMID, H. S. (1912): Mica; its occurrence, exploitation, and uses, 2nd ed. *Canada Mines Br., Pub.* **118**.
- WEAVER, C. E., WAMPLER, J. M. & PECUIL, T. E. (1967): Mössbauer analysis of iron in clay minerals, *Science*, **156**, 504-508.

*Manuscript received October 28, 1969, emended November 27, 1969.*