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The Mössbauer spectrum of a ferrian muscovite and its implications in the assignment of sites in dioctahedral micas

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SUMMARY. A muscovite that contains iron almost entirely in the ferric form has been studied by Mössbauer spectroscopy. It is established that Fe^{3+} ions in the sites with *cis* hydroxyl groups have similar parameters in both muscovite and biotite. By assuming that Fe^{2+} ions will also have similar parameters for these sites in both minerals the Mössbauer results of other workers have been reinterpreted. This new interpretation, which is in complete agreement with the X-ray structural analysis of Radoslovich (1960), indicates that in muscovite the sites with *cis* hydroxyl groups are filled in preference to those with *trans* hydroxyls. These sites are occupied primarily by trivalent ions. There is possibly a preference for divalent ions by the unique sites with *trans* hydroxyl groups, but occupation of these sites appears to occur only when the other sites have been filled.

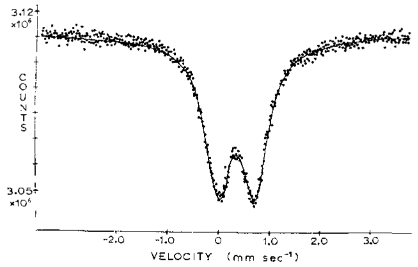
DETAILED Mössbauer spectra of two muscovites have been reported by Hogg and Meads (1970). In both of these spectra there was a large contribution from Fe^{2+} and the results were interpreted in terms of a large preference of ferrous iron for the unique octahedral site, which is usually considered to be vacant in dioctahedral micas. Other workers (e.g. Bowen *et al.*, 1969; Malden and Meads, 1967) have failed to resolve peaks from more than one octahedral site, possibly because of low iron contents, orientation effects, or insufficient time taken for the accumulation of the data. For one or more of these reasons no other assignments of sites in the Mössbauer spectra of dioctahedral micas have been made.

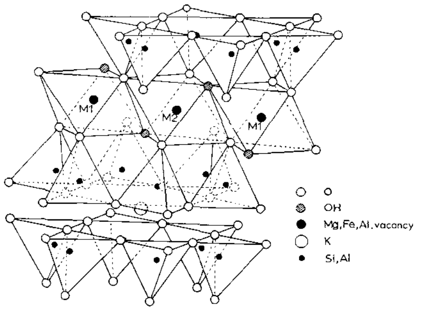
In this paper the Mössbauer results for a muscovite containing iron almost exclusively in the ferric form will be presented. Arguments will then be given which favour an alternative assignment to that of Hogg and Meads for the ferrous peaks in the Mössbauer spectra of muscovites. Finally, the ordering processes that occur in muscovite will be discussed in terms of this new assignment of the sites.

Experimental. The ferrian muscovite was obtained from Varkleivneset, Sogn, Norway (Askvik, 1972). Its X-ray powder pattern indicated a muscovite 2M structure, and chemical analyses gave 4·93 % Fe_2O_3 and 0·02 % FeO. Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer (Harwell Scientific Services, Didcot), employing an Ortec Model 6200 multichannel analyser operating in the multiscalar mode. Spectra were accumulated in 512 channels of the analyser. A ^{57}Co (in Pd) source of nominal strength 25 mCi was used with a xenon–methane proportional counter as γ-ray detector. Velocity calibration was carried out with a high-purity metallic iron foil using the data of Preston *et al.* (1962). The resulting spectra were fitted over 506 channels using a least-squares computer programme assuming Lorentzian line shapes. A parabolic base line was assumed and χ^2 was used as a goodness-of-fit parameter. For a statistically acceptable fit χ^2 is required to lie between the 1 % and 99 % limits of the χ^2 distribution, i.e. between about 430 and 575 for 500 degrees of freedom.

Absorbers (containing 3 mg iron per cm^2) were prepared by thoroughly grinding equal weights of the sample and alumina in an agate mortar. This was necessary in order to prevent preferential orientation of the crystals.

Results and discussion. The Mössbauer spectrum of the ferrian muscovite at room temperature is shown in fig. 1. A similar spectrum was obtained at 77 °K. Satisfactory values for χ^2 were obtained by fitting each spectrum to 1 doublet, values of 456 and 496 being obtained from the data from absorbers at room temperature and 77 °K respectively. The spectra are interpreted as arising from Fe^{3+} ions, there being a complete absence of any lines that might be attributable to Fe^{2+} (Bancroft *et al.*, 1967), as would be expected in this sample with a ratio Fe^{2+} : Fe^{3+} of only *ca.* 0·005. The results from these spectra are presented in Table I together with some results on different mica samples obtained by other workers.





FIGS. 1 and 2: FIG. 1 (left). Mössbauer spectrum of ferrian muscovite at room temperature. The unbroken line represents the computer fit to the data assuming only one doublet with equal area and half widths for both components. FIG. 2 (right). A simplified mica structure.

In this paper the octahedral sites in micas have been labelled according to the following convention: M1 is used to indicate the sites coordinated to four oxygens and two hydroxyl groups in a *cis* arrangement about the metal and M2 is used for the site with *trans* hydroxyl groups (see fig. 2). Thus this M1 site is comparable to the M1 site in amphiboles and the M2 site equivalent to the amphibole M3 (see, e.g., Deer *et al.*, 1963). This convention has been used in the past by Goodman and Wilson (1973) and by Yassoglou *et al.* (1972). However, the opposite convention, using M2 for the site with *cis* hydroxyls and M1 for the site with *trans* hydroxyls, has been used by Annersten (1974); in Table I his results are presented using the former notation.

In the precise X-ray structural analysis of a muscovite containing 2·29 % Fe_2O_3 (Radoslovich, 1960), the octahedral cations were shown to occur almost exclusively in the M1 sites with the M2 sites vacant. The mean metal–oxygen distance for the M1 sites was measured by Radoslovich as 1·95 Å, but the mean vacancy–oxygen distance for the M2 sites was appreciably higher at about 2·2 Å. On the basis of Radoslovich's results the Fe^{3+} in the muscovite studied in this work must be assigned to the M1 sites. Similar parameters (Table I) were obtained by Goodman and Wilson (1973) for Fe^{3+} in the same sites in a series of weathered biotites, although in the unweathered sample it was not possible to separate and distinguish the Fe^{3+} lines from the two types of octahedral site. Annersten (1974) needed Fe^{3+} ions in both types of octahedral site to obtain satisfactory computer fits of the spectra from a series of natural biotites. However, in all his samples a large percentage of the total iron was in the Fe^{2+} form and in these circumstances it is not possible to obtain very accurate values for the Fe^{3+} parameters for the two sites where the lines are not clearly resolved. The values quoted for Annersten's samples in Table I for the quadrupole splitting, Δ, are less and the corresponding values for the isomer shifts, δ, are greater than those in the paper referred to above (Goodman and Wilson, 1973). Similar values to those obtained in this work have been reported for the Fe^{3+} component in muscovites (Bowen *et al.*, 1969; Hogg and Meads, 1970), but in all of these samples there was appreciable Fe^{2+} content. These authors used one Fe^{3+} component in their computer fits but were unable to decide whether this iron was in one or both sites in the structure because of the difficulty in accurately determining the line shapes.

In view of the similarity in the Mössbauer spectra of muscovites and biotites (Hogg and Meads, 1970) and the establishment that Fe^{3+} in the M1 sites has similar parameters in both muscovites and biotites, it is reasonable to assume that Fe^{2+} will have similar parameters for the M1 sites in both minerals. Häggström *et al.* (1969), by working with an iron-rich biotite, found that the amount of Fe^{2+} with the larger value of Δ was more than one-third of the total octahedral sites, showing conclusively that this corresponds to Fe^{2+} in M1 sites. The Fe^{2+} component with the larger quadrupole splitting in muscovite should therefore be assigned to M1 sites. This is opposite to the assignment used by Hogg and Meads (1970), who assumed that divalent cations would be found mainly in the M2 sites, which had been shown by Radoslovich (1960) to be larger than the M1 sites in muscovite.

The assignments presented above raise some important questions concerning the ordering of the octahedral cations in muscovite. Veitch and Radoslovich (1963) have suggested that small trivalent ions such as Al^{3+} and Fe^{3+} will occupy preferentially the smaller site (in this case M1), and divalent ions such as Fe^{2+} and Mg^{2+} will occupy the larger site (M2). The results from this work confirm that Fe^{3+} is found preferentially in the M1 sites, but, if the assignments proposed above for Fe^{2+} are used with the results of Hogg and Meads, then there is also appreciably more Fe^{2+} in the M1 than in the M2 sites in both of their muscovites. Also, the Mössbauer parameters for both M1 and M2 sites in muscovite are similar to those for the same sites in biotite, in spite of the differences in site sizes determined by X-ray diffraction (see e.g. Radoslovich (1960) for muscovite; Donnay *et al.* (1964) for ferriannite, a trioctahedral mica that should have similar parameters to biotite for the octahedral layer). It would appear that the large differences in size of the M1 and M2 sites determined by X-ray diffraction are principally the result of the different electrostatic interactions occurring when octahedral positions are occupied by a trivalent ion or a vacancy and that these differences in size are locally removed when the sites are occupied by Fe^{2+}.

TABLE I. *Mössbauer parameters for some muscovites and biotites*

Sample	Temp. (°K)	Fe^{3+}						Fe^{2+}					
		M1			M2			M1			M2		
		Δ	δ	%	Δ	δ	%	Δ	δ	%	Δ	δ	%
Sogn muscovite *	298	0·724 (0·003)	0·361 (0·002)	100	—	—	—	—	—	—	—	—	—
Sogn muscovite †	77	0·738 (0·004)	0·465 (0·002)	100	—	—	—	—	—	—	—	—	—
Muscovite 1 ‡	298	0·82**	0·34**	47**				3·02	1·15	43	2·25	1·13	11
Muscovite 2 ‡	298	0·74**	0·37**	72**				3·04	1·15	23	2·14	1·10	5
Rehiran biotite §	298	0·89** (0·03)	0·38* (0·02)	43** (2)				2·64 (0·02)	1·13 (0·01)	36 (3)	2·19 (0·04)	1·11 (0·01)	21 (3)
Rehiran biotite § partly oxidized	298	0·76 (0·05)	0·34 (0·03)	37 (5)	1·08 (0·12)	0·41 (0·06)	26 (5)	2·66 (0·01)	1·13 (0·01)	26 (1)	2·11 (0·03)	1·15 (0·01)	11 (1)
Rehiran hydrobiotite	298	0·72 (0·02)	0·35 (0·01)	41 (5)	1·23 (0·11)	0·37 (0·03)	33 (6)	2·75 (0·04)	1·12 (0·02)	18 (1)	1·98 (0·04)	1·15 (0·02)	8 (1)
Biotite 1 ‖	298	0·50	0·43	9	1·02	0·41	9	2·56	1·06	41	2·10	1·03	40
Biotite 5 ‖	298	0·65	0·46	7	1·17	0·51	13	2·58	1·05	46	2·21	1·03	35
Biotite A ¶	298	0·89 (0·02)	0·39 (0·01)	33 (3)	—	—	—	2·65 (0·01)	1·12 (0·01)	38 (4)	2·31 (0·03)	1·11 (0·01)	29 (5)
Biotite B ¶	298	0·84 (0·04)	0·36 (0·02)	30 (2)	—	—	—	2·65 (0·02)	1·13 (0·01)	39 (4)	2·27 (0·03)	1·10 (0·02)	31 (5)

Δ = quadrupole splitting in mm sec^{-1}.

δ = isomer shift relative to iron metal in mm sec^{-1}.

% refers to the percentage of the total iron in this site.

Numbers in brackets correspond to one standard deviation.

* This work—full width at half height = 0·63 (0·01) mm sec^{-1}.

† This work—full width at half height = 0·64 (0·01) mm sec^{-1}.

‡ Hogg and Meads (1970)—these results have been tabulated in accordance with the assignments proposed in the current paper.

§ Goodman and Wilson (1973).

‖ Annersten (1974)—these results have been tabulated in accordance with the convention used in the current paper.

¶ B. A. Goodman and F. W. D. Woodhams—unpublished results.

** It was assumed by the authors of these papers that these values represent a weighted average of the contributions from both M1 and M2 sites.

The muscovites 1 and 2 in the paper by Hogg and Meads (1970) can be formulated $R_a^+(\mathrm{Si}_{6\cdot16}\,R^{3+}_{1\cdot84})(R^{3+}, R^{2+})_b\mathrm{O}_{20}(\mathrm{OH})_4$, where for sample 1 $a = 1{\cdot}87$, $b = 4{\cdot}05$, and $R^{2+} = 0{\cdot}23$, with $\mathrm{Fe}^{2+} = 0{\cdot}13$ and $\mathrm{Fe}^{3+} = 0{\cdot}24$; for sample 2 $a = 1{\cdot}80$, $b = 4{\cdot}15$, and $R^{2+} = 0{\cdot}44$, with $\mathrm{Fe}^{2+} = 0{\cdot}10$ and $\mathrm{Fe}^{3+} = 0{\cdot}37$. Using the assignments discussed above and the data of Hogg and Meads, the area ratios determined by Mössbauer spectroscopy for M1/M2 are 3·9 and 4·6, for samples 1 and 2 respectively. If Fe^{2+} is representative of the divalent ions the Mössbauer results indicate that about 2·3 % in sample 1 and 4 % in sample 2 of the M2 sites are occupied by divalent ions. If the M1 sites are completely filled then the M2-site occupancy predicted from the analytical results is 0·05 for sample 1 and 0·15 for sample 2, i.e. about 2·5 % and 7·5 % respectively. The percentage errors involved in both the Mössbauer area measurements for overlapping lines and the analytical determination of $(b-4{\cdot}0)$ for these muscovites must be high. It does, however, appear that an appreciable amount of the M2 sites that are occupied contain divalent ions. The ordering processes in muscovite can then be summarized thus: the M1 sites are filled preferentially; occupation of the M2 sites occurs if there are cations in excess of the requirements of the M1 sites; and of the occupied sites divalent cations may be concentrated in the M2 sites and trivalent cations in the M1 sites.

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REFERENCES

Annersten (H.), 1974. *Amer. Min.* **59,** 143.

Askvik (H.), 1972. *Norges geol. undersøk.* **273,** 7.

Bancroft (G. M.), Maddock (A. G.), and Burns (R. G.), 1967. *Geochimica Acta,* **31,** 2219.

Bowen (L. H.), Weed (S. B.), and Stevens (J. G.), 1969. *Amer. Min.* **54,** 72.

Deer (W. A.), Howie (R. A.), and Zussman (J.), 1963. *Rock Forming Minerals,* **2.** Longmans (London).

Donnay (G.), Morimoto (N.), Takeda (H.), and Donnay (J. D. H.), 1964. *Acta Cryst.* **17,** 1969.

Goodman (B. A.) and Wilson (M. J.), 1973. *Min. Mag.* **39,** 448.

Häggström (L.), Wappling (R.), and Annersten (H.), 1969. *Chem. Phys. Letts.* **4,** 107.

Hogg (C. S.) and Meads (R. E.), 1970. *Min. Mag.* **37,** 606.

Malden (P. J.) and Meads (R. E.), 1967. *Nature,* **215,** 844.

Preston (R. S.), Hanna (S. S.), and Heberle (J.), 1962. *Phys. Rev.* **128,** 2207.

Radoslovich (E. W.), 1960. *Acta Cryst.* **13,** 919.

Veitch (L. G.) and Radoslovich (E. W.), 1963. *Amer. Min.* **48,** 62.

Yassoglou (N. J.), Nobeli (C.), Kostikas (A. J.), and Simopoulos (A. C.), 1972. *Soil Sci. Soc. Amer. Proc.* **36,** 520.

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