

## A study of the weathering of a biotite using the Mössbauer effect

B. A. GOODMAN AND M. J. WILSON

The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, AB9 2QJ

**SUMMARY.** The behaviour of iron in the weathering of biotite in a sedentary soil profile developed on appinite has been investigated using the Mössbauer effect. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in sites with *cis* and *trans* hydroxyl groups were observed at various stages in the weathering sequence. The results indicate that there is little or no ordering of the octahedral cations in the fresh biotite and hydrobiotite, but in the more weathered interstratified vermiculite-chlorite samples  $\text{Fe}^{3+}$  concentrates in the more distorted sites. No evidence was obtained for the presence of an anisotropic recoil-free fraction.

IN the laboratory, biotite can be readily converted to vermiculite by a simple cation-exchange process involving replacement of interlayer  $\text{K}^+$  by a more highly hydrated cation such as  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ . However, under natural conditions the weathering of biotite is more complex since weathered biotites, vermiculitized to varying degrees, are invariably more highly oxidized than fresh flakes separated from related parent rock. The octahedral sheet is therefore affected. Because of the importance of the degree of oxidation of biotites for potassium retention in the soil (Barshad and Kishk, 1968; Robert and Pedro, 1968), the weathering reactions of the mineral have been investigated in detail.

Previous work (Wilson, 1970) on the weathered biotite in a sedentary soil profile from Rehiran, Inverness-shire, identified several distinct stages of weathering. Biotite in the bedrock (appinite, an ultrabasic biotite-hornblende rock) is first transformed into hydrobiotite in the *C* horizon and then into interstratified vermiculite-chlorite in the *B* horizon. The brucite interlayers subsequently tend to break down in the more acidic *A* horizon yielding a vermiculitic product. The initial biotite to hydrobiotite transition is characterized by loss of iron and extensive oxidation, as was indicated by chemical analysis, by decrease in the  $\beta\gamma$  refractive index, by development of vacancy bands in the IR spectra, and by a slight decrease in the *b* crystallographic axis. There was some evidence that part of the iron removed from the octahedral sheet may be retained in the interlayer region in the form of amorphous oxides.

The behaviour of iron in these weathering reactions has now been investigated in more detail using Mössbauer spectroscopy, a technique that provides complete selectivity for the  $^{57}\text{Fe}$  nucleus. The isomer shift,  $\delta$  (which is proportional to the electron density at the iron nucleus), and the quadrupole coupling constant,  $\Delta$  (which is a measure of the electric field gradient at the nucleus), are sensitive to both the oxidation state of the iron and the nature of the bonding in which it is involved. Two  $\text{Fe}^{2+}$  and

one  $\text{Fe}^{3+}$  sites have been identified in unweathered biotites (Hogg and Meads, 1970; Häggström *et al.*, 1969) and weathered biotites have also been studied (Rice and Williams, 1969; Yassoglou *et al.*, 1972). In the present study the processes of weathering of biotite are followed through to a vermiculitic end product within one soil profile.

### *Experimental*

The biotite flakes (75–150  $\mu\text{m}$ ) were separated by hand-picking from fresh bedrock, partly oxidized bedrock, and from the C (35 to 37"), B (12 to 17"), and A (2 to 6") horizons of the Rehiran soil profile.

Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer using an Intertechnique SA41 400-channel analyser operating in the multiscalar mode. Spectra were accumulated as mirror images in the first and second 200 channels of the analyser. The electromechanical drive system was based on the design of Clark *et al.* (1967). A  $^{57}\text{Co}$  in Pd source of nominal strength 10 mCi was used with a xenon-methane proportional counter as  $\gamma$ -ray detector. Velocity calibration was carried out with high-purity metallic iron foil using the data of Preston *et al.* (1962).

The resulting spectra were fitted to a sum of two, three, or four doublets having Lorentzian line shapes using a least squares computer programme. The lines in each doublet were assumed to have equal area and width. A parabolic baseline was assumed and  $\chi^2$  was used as a goodness of fit parameter. For a statistically acceptable fit  $\chi^2$  is required to lie between the 1% and 99% limits of the  $\chi^2$  distribution, i.e. between about 138 and 234 for spectra with 186 degrees of freedom.

Absorbers containing a total concentration of iron of *c.* 3  $\text{mg}\cdot\text{cm}^{-2}$  were prepared for Mössbauer absorption measurements by either of the following methods: grinding the mineral with alumina under alcohol in an agate mortar for *c.* 10 min and, after allowing the alcohol to evaporate, transferring the powder to a perspex holder; or grinding the mineral alone under alcohol for *c.* 15 min and after allowing the alcohol to evaporate, adding 100 mg spectroscopic quality polyethylene powder. The sample was then thoroughly mixed and pressed into a 13 mm diameter disk with a load of about 60 MN. In each case the method was adequate to prevent preferential alignment of platelets in the absorbers.

Samples were analyzed chemically for FeO and  $\text{Fe}_2\text{O}_3$  using a modification of the method of Wilson (1960).

### *Results and Discussion*

The Mössbauer spectra of the fresh and weathered biotite samples are shown in fig. 1. In all cases unacceptable values for  $\chi^2$  were obtained when the spectra were fitted to two doublets, values of 572, 704, 567, 362, and 318 being obtained for the spectra in fig. 1 *a–e*, respectively. The fresh biotite and the interstratified vermiculite-chlorite samples gave acceptable values for  $\chi^2$  when the spectra were fitted with three doublets (Table I and fig. 1 *a, d, and e*). However, with the partly oxidized bedrock biotite and hydrobiotite  $\chi^2$  values of 363 and 286, respectively, were obtained and it was thus necessary to use four doublets to obtain acceptable fits to the spectra (Table I and fig. 1 *b and c*). The computed Mössbauer parameters for the accepted models

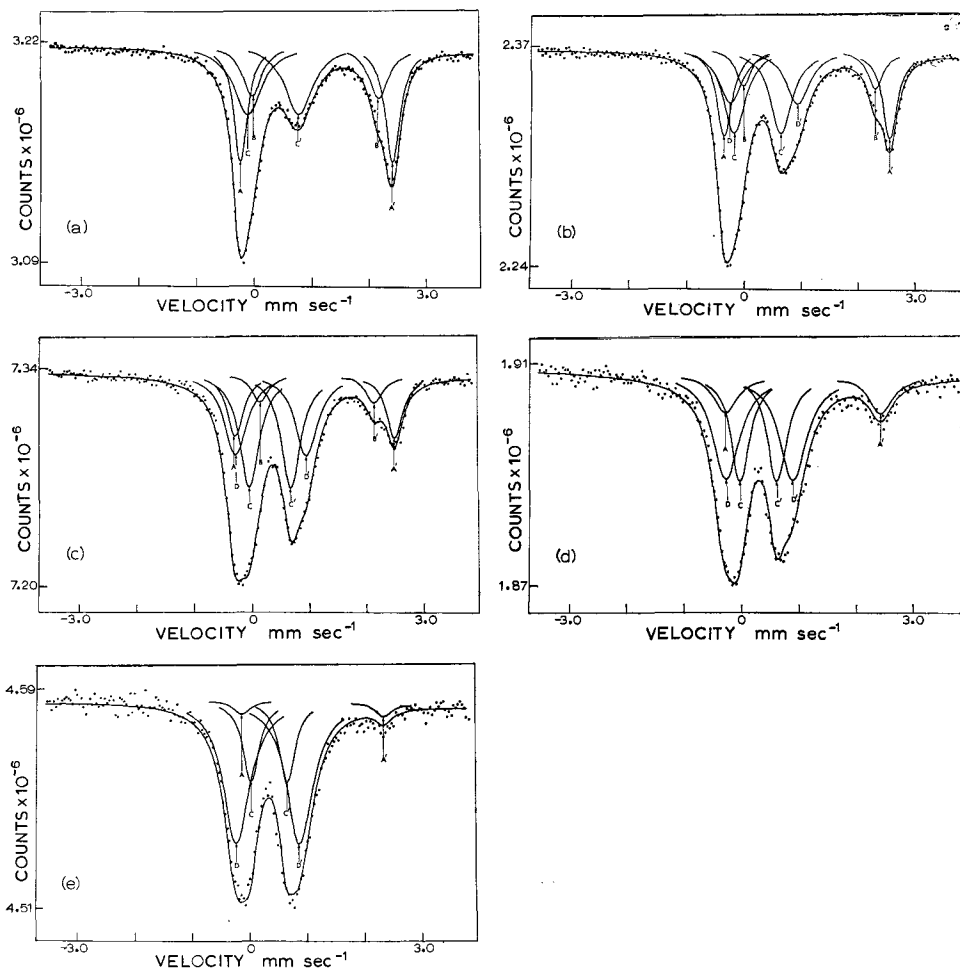


FIG. 1. Mössbauer spectra of fresh and weathered biotite samples (a) fresh biotite (bedrock), (b) partly oxidized biotite (bedrock), (c) hydrobiotite (C horizon), (d) interstratified vermiculite-chlorite (B horizon), and (e) interstratified vermiculite-chlorite (A horizon).

together with the chemically obtained iron contents are shown in Table I, where  $\Delta$ ,  $\delta$ , and  $\Gamma$  refer to the quadrupole splittings, isomer shifts, and line widths, respectively. The errors, which are quoted in brackets, include both standard deviation and covariance contributions.

*Assignment of oxidation states.* Oxidation states have been assigned to the various iron components using the interpretations of other workers (e.g. Bancroft *et al.*, 1967) on the basis of the magnitudes of the isomer shifts,  $\delta$ , and quadrupole splittings,  $\Delta$ . Thus, in the spectra shown in fig. 1 the doublets  $AA'$  and  $BB'$  are assigned to  $\text{Fe}^{2+}$  and the doublets  $CC'$  and  $DD'$  to  $\text{Fe}^{3+}$ . Table I shows that the fresh biotite yields

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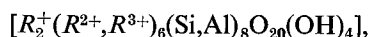
TABLE I. Computed Mössbauer results for fresh and weathered biotites (M1 and M2 refer to the octahedral sites with cis and trans co-ordinated hydroxyl groups, respectively)

Sample	Fe <sup>2+</sup>						Fe <sup>3+</sup>						χ <sup>2</sup>	
	Chem. Fe <sup>2+</sup>		M1		M2		Chem. Fe <sup>3+</sup>		M1		M2			
	Δ†	δ†*	Γ†	%‡	Δ†	δ†*	Γ†	%‡	Δ†	δ†*	Γ†	%‡		
Fresh biotite	7.47 (0.02)	1.13 (0.01)	0.30 (0.01)	36 (3)	2.19 (0.04)	1.11 (0.01)	0.40 (0.03)	21 (3)	4.23	0.89 (0.03)	0.38 (0.02)	0.60 (0.02)	43 (2)	253
Partly oxidized biotite (bedrock)	2.66 (0.01)	1.13 (0.01)	0.29 <sup>x</sup> (0.01)	26 (1)	2.11 (0.03)	1.15 (0.01)	0.20 <sup>x</sup> (0.01)	11 (1)		0.76 (0.05)	0.34 (0.03)	0.42 (0.02)	37 (5)	245
Hydrobiotite (C horizon)	2.37	2.75 (0.04)	1.12 (0.02)	0.33 <sup>x</sup> (0.02)	18 (1)	1.98 (0.04)	0.33 <sup>x</sup> (0.02)	8 (1)	6.68	0.72 (0.02)	0.35 (0.01)	0.41 (0.02)	41 (5)	185
Interstratified vermiculite- chlorite (B horizon)	1.15	2.71 (0.18)	1.13 (0.08)	0.50 (0.06)	15 (2)				7.06	0.64 (0.03)	0.37 (0.01)	0.41 (0.03)	35 (9)	237
Interstratified vermiculite- chlorite (A horizon)	1.21	2.51 (0.45)	1.15 (0.22)	0.34 (0.03)	5 (1)				6.93	0.63 (0.03)	0.37 (0.01)	0.34 (0.03)	28 (8)	241

† all values in mm.sec<sup>-1</sup>.  
 \* isomer shifts quoted relative to Fe metal.  
 ‡ % refers to the percentage of the total Fe.  
 x half widths constrained to be equal.  
 The errors quoted in brackets include standard deviations and covariance contributions.

parameters consistent with two  $\text{Fe}^{2+}$  components and one  $\text{Fe}^{3+}$  component. For partly oxidized biotite and hydrobiotite an additional  $\text{Fe}^{3+}$  component is evident, whilst in the interstratified vermiculite–chlorites only one  $\text{Fe}^{2+}$  component remains compared with two  $\text{Fe}^{3+}$  components.

*Assignment to sites in the biotite structure.* The octahedral cations of micas may occupy two different types of site (Wyckoff, 1960), one designated  $M_1$  where the hydroxyl groups are arranged adjacent to one another (*cis*), and one designated  $M_2$  in which the hydroxyl groups are opposite (*trans*). In one formula unit



where  $R^+$ ,  $R^{2+}$ , and  $R^{3+}$  represent mono-, di-, and tri-valent metals, respectively, there are four  $M_1$  and two  $M_2$  sites. Häggström *et al.* (1969) from their work on a biotite with high iron content and on a synthetic annite found the number of  $\text{Fe}^{2+}$  sites per formula unit to be greater than two for the component with the larger value of  $\Delta$ , showing conclusively that this corresponds to the  $M_1$  site. Thus in fig. 1 peaks  $AA'$  are assigned to the  $M_1$  sites and peaks  $BB'$  to the  $M_2$  sites. Ingalls (1964) has shown that for 6-coordinated high-spin  $\text{Fe}^{2+}$   $\Delta$  decreases from about  $3.7 \text{ mm. sec}^{-1}$  with increasing distortion from octahedral symmetry, and for high-spin  $\text{Fe}^{3+}$   $\Delta$  increases from  $0 \text{ mm. sec}^{-1}$  with increasing distortion. Thus the  $\text{Fe}^{3+}$  component with the larger  $\Delta$  (peaks  $DD'$ ) is assigned to  $M_2$  and that with the smaller  $\Delta$  (peaks  $CC'$ ) to  $M_1$ . These assignments are consistent with the structure of the trioctahedral mica phlogopite, where the bond lengths and angles are similar for octahedral cations with *cis* and *trans* combinations of hydroxyl groups (Donnay *et al.*, 1964), together with the observation that the lattice contribution to the electric field gradient is greater for *trans* than for *cis* combinations of groups (see e.g. Berrett and Fitzsimmons, 1967). Hogg and Meads (1970) and Yassoglou *et al.* (1972) have used the opposite assignment based on the structure established for the dioctahedral mica muscovite, where the octahedral cations having *cis* hydroxyl groups are in a much more distorted environment than those having a *trans* combination (Radoslovich, 1960). From this assignment Hogg and Meads (1970) wrongly concluded that the  $\text{Fe}^{2+}$  ions in biotite are ordered with the  $M_2$  site being favoured.

*Interpretation of spectra.* In the fresh biotite the presence of  $\text{Fe}^{2+}$  can be seen in both  $M_1$  and  $M_2$  sites (fig. 1a,  $AA'$  and  $BB'$ , respectively), with  $M_1$  being predominant. Only one  $\text{Fe}^{3+}$  component (fig. 1a,  $CC'$ ) was identified from the computer fit to the data. The large line widths,  $\Gamma$ , however, compared with those obtained from  $\text{Fe}^{3+}$  in the  $M_1$  site in the other samples studied indicate that more than one site is occupied. Both the partly oxidized biotite separated from the bedrock and the hydrobiotite contain two  $\text{Fe}^{2+}$  components but these are much less abundant than in the fresh biotite. In addition, two identifiable  $\text{Fe}^{3+}$  components (fig. 1b and c,  $CC'$  and  $DD'$ ) become evident, both yielding parameters consistent with octahedral coordination (Bancroft *et al.*, 1967). The interstratified vermiculite–chlorite samples are so low in ferrous iron that statistically acceptable fits to the data are obtained with only one  $\text{Fe}^{2+}$  component in the  $M_1$  site. However, the large width and the asymmetry of the

line at  $A'$  in fig. 1*d* indicates that probably both sites are occupied. Table I also shows that during the later stages of weathering the amounts of the  $\text{Fe}^{3+}$  component in the  $M_2$  sites increase relative to  $M_1$ . This apparent ordering, however, may be partly accounted for by three other factors:

It is possible that the  $\text{Fe}^{3+}$  ions and vacant sites produced during biotite weathering may be associated with each other in the octahedral sheet (Krzanowski and Newman, 1972). This could lead to an increase in the lattice contribution to the electric field gradient at the  $\text{Fe}^{3+}$  ions. Thus the broad component (fig. 1,  $DD'$ ) with  $\Delta \sim 1.2$  mm.  $\text{sec}^{-1}$ , assigned to  $\text{Fe}^{3+}$  in  $M_2$  sites, may include contributions from  $\text{Fe}^{3+}$  in  $M_1$  sites with an adjacent vacant octahedral site. This effect, however, may not be significant because most of the  $\text{Fe}^{2+}$  has been oxidized by the time the hydrobiotite stage in the profile has been reached, with no apparent concentration of  $\text{Fe}^{3+}$  in the  $M_2$  sites.

Some small discrete grains of an iron oxide mineral having the visual appearance of hematite were observed on the surfaces of some of the weathered samples. However, no lines from any magnetic species were observed in the Mössbauer spectra of any of the samples and it is thus unlikely that the contributions from these grains are significant.

Microcrystalline iron oxide may be present in the interlayer spaces, and might be superparamagnetic with a value of  $\Delta \geq 1$  mm.  $\text{sec}^{-1}$  (see, e.g. Kündig *et al.*, 1967), thus contributing to the broad resonance with  $\Delta \sim 1.2$  mm.  $\text{sec}^{-1}$ . By virtue of its microcrystalline size any interlayer iron would probably have a low  $f$ -factor (Van Wieringen, 1968), and it is significant in this respect that Helsen *et al.* (1970) could not observe any Mössbauer resonance from the adsorbed iron in montmorillonite saturated with  $^{57}\text{Fe}^{3+}$ . Also because the amount of iron present in the interlayer spaces is likely to be low compared with that in the structure the contributions to the spectrum from this iron will be minimal.

It is concluded, therefore, that, despite the complicating factors mentioned above, there is an ordering effect in the interstratified vermiculite–chlorite samples with  $\text{Fe}^{3+}$  concentrated in the  $M_2$  sites, although a progressive change towards a dioctahedral structure cannot be discounted.

*Comparison with other studies.* It is interesting to compare the results presented here with two other Mössbauer studies of biotite weathering. Rice and Williams (1969) studied a weathering profile in which comparatively little oxidation had occurred. Only one  $\text{Fe}^{2+}$  component in the  $M_1$  site was observed, with no octahedrally coordinated high-spin  $\text{Fe}^{3+}$  ions. Weathering resulted in a reduction in  $\text{Fe}^{2+}$  content and the appearance of a new  $\text{Fe}^{3+}$  component characteristic of a high-spin 6-coordinated species. The profiles studied by Yassoglou *et al.* (1972) contained hydrobiotite in the bedrock and only a small amount of  $\text{Fe}^{2+}$  was present indicating that appreciable weathering had already taken place. Two  $\text{Fe}^{3+}$  components were observed throughout the weathering profile but, in contrast to the present results, no appreciable changes in relative abundances were found. In both these papers a Goldanskii–Karyagin effect—i.e. anisotropy of the recoil-free fraction (Goldanskii *et al.*, 1963)—was assumed to be present in the data analyses in order to explain the unequal areas computed for

the components of the doublets. Hogg and Meads (1970), however, demonstrated the absence of this effect in their samples by performing experiments at 4.2 °K as well as at room temperature, and in the present work acceptable values of  $\chi^2$  were obtained by constraining the widths and areas of the doublets to equality.

### Conclusions

The Mössbauer results described above have further elucidated the process of oxidative weathering of biotite in the Rehiran soil. Results for the fresh biotite are consistent with there being little or no ordering of either Fe<sup>2+</sup> or Fe<sup>3+</sup> within the structure. The biotite to hydrobiotite transition is characterized by rapid and extensive oxidation of Fe<sup>2+</sup> in both *M1* and *M2* sites, although oxidation is not as complete as was previously concluded (Wilson, 1970). The remaining Fe<sup>2+</sup> is slowly oxidized during the change from hydrobiotite to a more vermiculitic product. Weathering results in the loss of ferrous iron from both *M1* and *M2* sites at a similar rate, indicating that oxidation does not take place preferentially at any one site, although ferric iron does appear to concentrate in the more distorted sites of the highly weathered samples.

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