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A Mössbauer study of biotite weathering

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SUMMARY. Fresh and weathered biotites have been studied using Mössbauer, chemical, and X-ray analytical techniques. In the Mössbauer spectra the complete interference of both low-spin ferric lines by one of the high-spin ferrous lines and the existence of high-spin ferric iron in the weathered biotite has been demonstrated. In view of this interference, which appears to be common, allowances must be made in spectral interpretation if chemical analysis reveals ferric iron to be present in detectable amounts. Hypothetical extension of the weathering trends observed suggests that high-spin ferric iron is the only stable iron species in the end product.

During weathering marked loss of ferrous iron occurs, whereas the ferric iron content remains approximately constant. As a result of the instability of ferrous iron in the weathering environment there is a significant rearrangement of the octahedral layer.

DURING a general geochemical study of the breakdown of the Carnmenellis Granite (Cornwall) from a deep weathering profile, the first observable change was considerable iron staining. In slightly more altered material physical disintegration of biotite occurred. Since this process appeared to be important biotites were separated from various rock-breakdown stages and analysed by chemical and X-ray techniques. The major chemical change was obviously in the iron content, which suggested that a Mössbauer study could provide useful further information as it has been shown to be sensitive to the oxidation state of iron and particularly its co-ordination number (Boyle and Hall, 1962).

Samples were obtained from a weathering profile in the Bosahan quarry (O.S. 190 734,034), which is five miles WSW. of Falmouth. The sample numbers are FR1B (fresh biotite) and 8B 30/50 (weathered biotite). Intermediate stages were studied but were only important in that they show intermediate properties and hence it is reasonable to link alteration with weathering.

Experimental. The theory behind the Mössbauer effect has been described exhaustively in the recent literature (e.g. Gol'danskii, 1966).

A 3 mc ^{57}Co in palladium source was used to obtain the Mössbauer absorption spectra. This source is monoenergetic and combines the advantages of a reasonably high recoiless fraction and a very narrow line width. Absorbers containing approximately 50 mg/cm^2 powdered biotite were used. The 14·4 keV γ-rays to the ground state of Fe^{57} were detected using a xenon-methane filled proportional counter, the counts being stored in an R.I.D.L. 400 channel analyser operating in the time mode. Total counts in excess of $2{\cdot}8\times10^6$ per channel were recorded for each spectrum. Used in conjunction with a constant acceleration

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drive system the analyser produced a linear velocity scale directly. Such a spectrometer accumulates two spectra, one being the mirror image of the other, and in order to make full use of the data these are combined prior to analysis.

The resulting spectra were then fitted to Lorentzian line shapes using the Atlas computer at Chilton. In view of the fact that the experimental spectra are not always visually resolvable into separate Lorentzian components, it is necessary to try fitting varying combinations of lines, and the combination giving the lowest value of the statistic χ^2 was accepted as the best fit. It is interesting to note that significantly better fits are obtained if the components of each quadruple doublet are allowed to have different intensities. An asymmetry in the splitting is possible even for powdered samples, as indicated by Gol'danskii (1966), and is attributed to an anisotropy in the recoilless fraction. Such an asymmetry was first observed for tin compounds (Gol'danskii, Makarov, and Khrapov, 1963), and has since been identified in iron compounds (King, Herber, and Wertheim, 1964).

The values of χ^2 obtained are, however, higher than those expected for ideal or perfect fits, and this can be due to several factors as indicated by Bancroft *et al.*, 1967. In the present spectra the main contribution to high χ^2 values is the fact that the experimental absorption lines are not exactly Lorentzian in shape. This becomes obvious when the actual deviation between the experimental points and the Lorentzian fit is plotted against velocity. Such a plot shows no obvious extra absorption lines but does show a noticeable deviation from Lorentzian line shape. It should also be remembered that the absorption due to small traces of iron present in various sites will not be resolvable, and will therefore contribute to the measured χ^2.

Chemical and X-ray analysis. The biotites were extracted from the weathered and fresh samples by a combination of the standard techniques for crushing for the fresh, sedimentation for the weathered (Brewer, 1964), and magnetic separation for both samples.

Selection of the 30/50 μ fraction from the weathered sample ensured as far as possible that the biotite would be well weathered. In case the hypochlorite/dithionite treatment employed during sedimentation had affected the ferrous/ferric ratio of the weathered biotite, a fresh biotite (FR1B) was subjected to the same treatment. No appreciable change was observed (before, Fe_2O_3 4·35, FeO 18·82 %; after, Fe_2O_3 3·66, FeO 17·60 %).

Standard rapid methods of silicate analysis, following Shapiro and Brannock (1952) or modifications of their methods were used for most elements.

Diffractometer tracings were obtained from a Phillips PW 1049/01 diffractometer using Cu-$K\alpha$ radiation (Ni-filtered with pulse height analysis). The X-ray diffractograms of the two specimens were virtually identical with d_{001} $10{\cdot}1_0$, d_{060} $1{\cdot}53_0$ Å.

Mössbauer results. The spectra obtained for the two specimens are shown in fig. 1 and their Mössbauer parameters listed in table II. The most striking difference between the two spectra is the appearance of a new line (3) in fig. 1 (*b*). The relative intensities of lines 1 and 2 (as assessed from peak areas) changes from 1·4 (fresh) to 1·8 (weathered). Lines 1 and 2 are also significantly asymmetrical; this cannot be due to non-linearity of scan as a perfectly symmetrical line was obtained using a stainless steel single-line absorber.

Any interpretation of these spectra must take into account the ferric iron content revealed by chemical analysis, which is within the sensitivity of the apparatus. Several models were tried for both spectra, their relative merit being assessed by the value of χ^2 and the correlation between the ferrous/ferric ratios obtained by computer and chemical analysis. The computer ratio was calculated by summing the intensities of the lines for each oxidation state and taking the ratio of the two totals. The

Mössbauer parameters for the most acceptable model in each case are given in table II, and a pictorial representation in fig. 2 (*a*) and (*b*).

Interpretation. Previous Mössbauer investigations of biotite were of an exploratory nature on material of unspecified composition (Pollak *et al.*, 1962; Weaver *et al.*, 1967; Lefelhocz *et al.*, 1967; Herzenberg *et al.*, 1968); in all cases the observed spectra were considered to result from two similar asymmetric doublets, which were derived from ferrous ions occupying the two types of octahedral site (M_1 and M_2) in equal numbers (see Wyckoff, 1960, for details of the biotite structure). The spectrum obtained by Weaver *et al.* (1967) also contained a small peak at 0·49 mm/sec. This they attributed to ferric iron in octahedral co-ordination.

TABLE I. *Major element analysis of the fresh and weathered biotites and numbers of ions on the basis of 22 oxygen* (*20*(O)+*4*(OH+F))

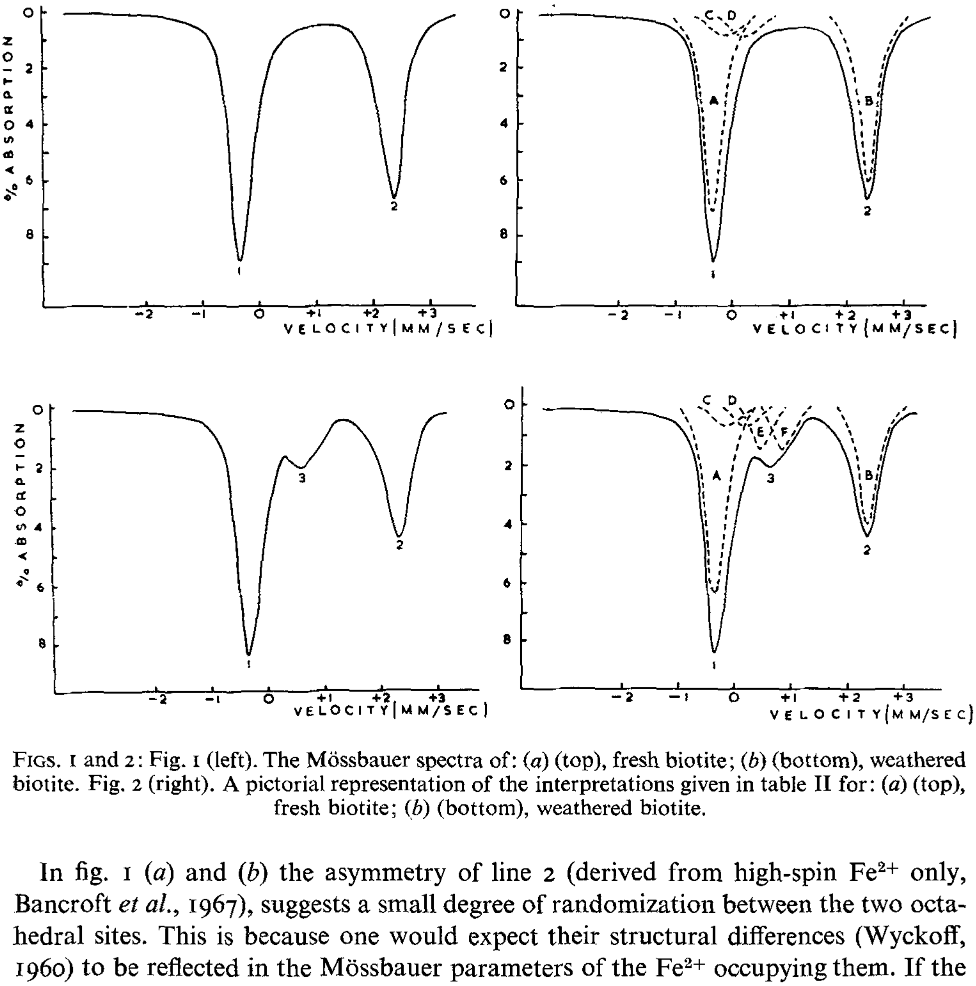
	Fresh	Weathered		Fresh		Weathered	
SiO_2	35·54	34·99	Si	5·29	8·00	5·31	8·00
Al_2O_3	21·53	23·39	Al^{iv}	2·71		2·69	
Fe_2O_3	4·35	5·67	Al^{vi}	1·07	5·36	1·49	5·02
FeO	18·82	10·86	Ti	0·28		0·19	
MgO	5·20	5·68	Fe^{3+}	0·49		0·65	
CaO	tr.	1·59	Fe^{2+}	2·34		1·38	
Na_2O	0·37	0·62	Mn	0·03		0·03	
K_2O	9·26	7·47	Mg	1·15		1·28	
TiO_2	2·47	1·64	Ca	tr.	1·86	0·24	1·86
P_2O_5	0·03	0·16	Na	0·10		0·18	
MnO	0·25	0·24	K	1·76		1·44	
H_2O^+	2·49	7·10	OH	2·78	3·14	3·63	4·00
H_2O^-	—		F	0·36		0·37	
F	0·77	(0·77)*	H_2O†	—		1·78	
	100·74	100·18					
F ≡ O	0·32	0·32					
	100·42	99·86					

* Assumed to be the same as the fresh material.
† Probably adsorbed or interlayer.

The Mössbauer parameters previously observed for ferrous and ferric iron in their various co-ordinations and spins have been tabulated by Bancroft *et al.* (1967). Accordingly, in fig. 1 (*a*) and (*b*), lines 1 and 2 can be ascribed mainly to high-spin Fe^{2+} in octahedral co-ordination. It seems therefore that the ferric lines must be completely concealed by line 1. The validity of this assumption has been considered justified by the close agreement between the ferrous/ferric ratio as derived by computer and by chemical analysis (table II). The parameters obtained for this extra doublet (lines C and D in table II and fig. 2 (*a*)) lie within the range of low-spin Fe^{3+} in octahedral co-ordination. The spectrum obtained by Weaver *et al.* (1967) is interesting, as it appears that in this case the low-spin ferric doublet is not entirely concealed.

The new line (3) in the spectrum of the weathered biotite represents a new closely spaced doublet (lines F and E in table 4 and fig. 2 (*b*)). This doublet is attributable to high-spin Fe^{3+} in octahedral co-ordination.

The total ferric iron content has remained roughly constant; the ratio high-spin: low-spin is about 1 : 1 (obtained by summing the intensities of each doublet and taking the ratio of the totals) in the weathered biotite. Therefore, there must have been a net gain of high-spin over low-spin Fe^{3+} during weathering.



FIGS. 1 and 2: Fig. 1 (left). The Mössbauer spectra of: (*a*) (top), fresh biotite; (*b*) (bottom), weathered biotite. Fig. 2 (right). A pictorial representation of the interpretations given in table II for: (*a*) (top), fresh biotite; (*b*) (bottom), weathered biotite.

In fig. 1 (*a*) and (*b*) the asymmetry of line 2 (derived from high-spin Fe^{2+} only, Bancroft *et al.*, 1967), suggests a small degree of randomization between the two octahedral sites. This is because one would expect their structural differences (Wyckoff, 1960) to be reflected in the Mössbauer parameters of the Fe^{2+} occupying them. If the occupation is unequal the effect of superposing two closely spaced lines of differing peak height would be one asymmetric line; note the extra width of line 2 compared with line 1 in table II. As the asymmetry is only slight it would appear that the majority of the Fe^{2+} is in one site. The ratio M_1:M_2 is 2:1 and Fe^{2+} occupies 2·34 out of the 6 available octahedral sites (see table I); thus it is possible that most of the Fe^{2+} is in the M_1 site.

To sum up, the vast majority of the iron in the fresh biotite occupies octahedral sites and is either high-spin Fe^{2+} or low-spin Fe^{3+}. In the weathered biotite there is an additional high-spin Fe^{3+} octahedral site. During weathering there appears to be a net gain of high-spin over low-spin Fe^{3+}.

TABLE II. *Mössbauer parameters for the fresh and weathered biotites* (a), *and for the most acceptable interpretations of the spectra derived from them* (b). *All measurements are at* 23 °*C. Posn., Position; I.S., Isomer Shift; Q.S., Quadrupole Splitting; W., Width; Com. and Che., Computer and Chemical Analysis respectively*

a						b						
Line	Posn. mm/sec	I.S. mm/sec	Q.S. (2ϵ) mm/sec	W. mm/sec		Line	Posn. mm/sec	I.S. mm/sec	Q.S. (2ϵ) mm/sec	W. mm/sec	Fe^{2+}/Fe^{3+}	
											Com.	Che.
Fresh biotite												
1	−0·05	+1·23	2·56	0·22	Fe^{2+} (high-spin)	A	−0·08	+1·24	2·63	0·22	4·5	4·8
2	+2·51			0·24		B	+2·56					
					Fe^{3+} (low-spin)	C	−0·07	+0·06	0·24	0·20		
						D	+0·18					
Weathered biotite												
1	−0·03	+1·24	2·54	0·23	Fe^{2+} (high-spin)	A	−0·06	+1·24	2·61	0·23	1·6	2·1
2	+2·51			0·24		B	+2·55					
	+0·84			0·30	Fe^{3+} (low-spin)	C	−0·10	+0·05	0·30	0·17		
						D	+0·20					
					Fe^{3+} (high-spin)	E	+0·25	+0·58	0·67	0·21		
						F	+0·92					

Isomer shifts have been quoted relative to the value of zero mm/sec for stainless steel.

Process and mechanism of weathering

The principal changes accompanying weathering as deduced from chemical and spectral data are: A marked loss of ferrous iron; a slight gain in ferric iron; and the location of ferric iron within a new octahedral site. Other chemical changes include an increase in the H_2O^+ content (the location of which is uncertain) and particularly a significant diminution of interlayer K_2O.

A hypothetical extension of the first change would result in a totally ferric phase. It is significant in this respect that the spectrum of 'weathered biotite' examined by Weaver *et al.* (1967) consisted of a single doublet (I.S. 0·28 mm/sec, Q.S. (2ϵ) 0·60 mm/sec). This was attributed to ferric iron in octahedral co-ordination, the Mössbauer parameters of which are very close to those of high-spin Fe^{3+} in the weathered specimen of the present study (I.S. 0·21 mm/sec, Q.S. (2ϵ) 0·67 mm/sec).

The octahedral layer, in particular, is evidently unstable in the weathering environment and undergoes rearrangement. Although obvious from chemical and Mössbauer considerations, this alteration affects neither basal nor 060 reflections as determined from simple diffractometer traces. Within the octahedral layer ferrous iron is the most unstable. It follows, therefore, that the presence of ferrous iron makes the octahedral layer unstable and is the principal factor controlling biotite alteration. Precisely why the ferrous iron is unstable is uncertain, but any mechanism of rearrangement must explain this. There are at least two possibilities: the activity of ferrous iron is very low in the oxidative weathering environment; this might instigate diffusion out from the Fe^{2+}-rich phase; oxidation within the weathering environment would maintain the activity low and the unstable situation; the loss of so much iron would cause strain in the lattice, hence the rearrangement. Alternatively, as the weathering environment is oxidizing and so electron deficient and ferrous ions provide a ready source of these, oxidation may occur within the lattice; to retain electrical neutrality, a third of the oxidized ferrous iron must be expelled causing strain and again rearrangement.

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