The Mössbauer spectra of several micas and related minerals

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SUMMARY. Well-resolved Mössbauer spectra of several dioctahedral and trioctahedral micas have been obtained and subjected to detailed computer analysis. Most of the spectra can be resolved into two ferrous quadrupole doublets and one ferric quadrupole doublet. In dioctahedral micas, ferrous iron is seen to occupy the larger, more symmetric octahedral site in preference to the smaller, less symmetric site, confirming predictions made on the basis of structure alone. In trioctahedral micas there is still a tendency for ferrous iron to occupy preferentially the more symmetric octahedral site even though the two octahedral sites are no longer distinguished by size. A lithium-rich biotite gives a spectrum typical of that expected from a mica with a zinnwaldite structure, but the spectrum of a more authenticated zinnwaldite could not be resolved sufficiently for detailed structural interpretation. The spectra of pyrophyllite and talc give results that can be related to the corresponding micas by considering their respective structural differences. In none of the micas studied was there evidence of ferric iron in tetrahedral coordination. The ferrous:ferric ratios obtained from the Mössbauer spectra do not always agree with the chemical values. In several cases the spectra show more ferrous iron than found chemically. It is suggested that the spectral values are more accurate, oxidation on chemical analysis being the most likely source of error.

THE Mössbauer spectra of various micas have been obtained by several authors (Pollak *et al.*, 1962; Herzenberg and Toms, 1966; Weaver *et al.*, 1967; Malden and Meads, 1967; Herzenberg *et al.*, 1968; Bowen *et al.*, 1969) but nowhere has a detailed analysis of the spectra in terms of mica structures been presented. This is probably due to the low iron content of many micas coupled with orientation effects, which give confusing spectra. Bowen *et al.* (1969) have obtained well-resolved spectra of several micas, but they found no evidence for more than one ferrous and one ferric quadrupole doublet, and have concentrated on the change in oxidation state of the iron in the micas under artificial weathering conditions.

Bancroft *et al.* (1967, 1968) have shown how detailed computer analysis of Mössbauer spectra in minerals can lead to accurate interpretations of the spectra in terms of crystal structure. Similar techniques have been applied here to well-resolved spectra of a number of micas and related sheet silicates, and the spectra interpreted in terms of structure and site occupation.

Sample description and preparation. Of the twelve sheet silicates investigated, five were

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supplied by English Clays, Lovering Pochin & Co. Ltd., St. Austell, Cornwall. These were the Lee Moor muscovite, the Trelavour and Tregarden biotites, the zinnwaldite, and the talc. The four micas are all derived from the granites of south-west England and all were received as fine powders, below 2 μm E.S.D (equivalent spherical diameter). The Lee Moor muscovite is reputed to contain about 15 % kaolinite, but this is not thought to influence the results significantly. The Trelavour biotite is a lithium-rich pegmatitic biotite, whereas the Tregarden biotite represents the common biotite of the south-west granite. The zinnwaldite and Trelavour biotite have been described

TABLE I. *Chemical analyses of sheet silicates, Nos. 3 and 4 by R. Ellis, Geol. Dept., University of Exeter, others by R. Masom and P. Willey of English Clays, Lovering Pochin and Co. Ltd.*

	1	2	3	4	5	6	8	9	10
SiO_2	45·77	45·35	44·69	43·88	40·82	35·43	38·90	49·80	52·62
TiO_2	0·41	0·49	0·69	0·50	2·22	3·36	0·36	0·30	0·15
Al_2O_3	33·80	32·13	30·84	30·64	15·75	17·51	22·00	20·70	31·01
Fe_2O_3	2·38	3·59	4·05	1·81	0·32	4·75	2·07	0·90	0·77
FeO	1·12	0·91	1·83	0·86	3·21	16·35	16·95	5·70	0·39
CaO	0·04	0·36	0·63	0·91	0·45	1·18	1·30	0·10	0·44
MgO	0·50	1·38	1·06	5·66	24·75	9·77	0·50	0·20	0·65
MnO	—	—	0·21	0·04	—	—	0·34	0·58	—
K_2O	9·08	9·31	10·93	10·37	8·83	7·64	9·32	10·30	9·10
Na_2O	0·46	0·70	0·57	0·75	1·35	0·47	0·33	0·26	0·31
Li_2O	0·34	—	—	—	—	—	1·49	4·10	—
H_2O	—	—	—	—	—	—	4·58	2·90	—
F	—	—	—	—	—	—	4·00	6·80	—
Ign.	6·10	5·13	—	—	2·19	3·42	—	—	4·13

1. Lee Moor muscovite.   2. Madagascar muscovite.   3. M2.
4. M1.   5. Indian phlogopite.   6. Aberdeen biotite.
8. Trelavour biotite.   9. Zinnwaldite.   10. Gilbertite.

by Cundy *et al.* (1960). The sample of talc was taken from a dark green-coloured block of Turkish origin. The Madagascar muscovite, the Aberdeen biotite, the phlogopite from Benares, India, and the Cumberland gilbertite were all obtained commerically as large single crystals or polycrystalline specimens. The micas M1 and M2 were obtained from the Geology Department of this University, but their origin is not known. The pyrophyllite was a sample of the material known as 'Wonderstone' believed to come from Sicily. The analyses of the samples, where available, are given in table I.

Bowen *et al.* (1969) have shown that unless the sample orientation of micas is made completely random, the spectra obtained have a pronounced asymmetry. We have used a randomizing technique similar to that described by Brindley and Kurtossy (1961) for randomizing kaolinites. The micas, ball milled and refined to below 10 μm E.S.D. where necessary, were slurried with a solution of 'Lakeside C' thermoplastic resin in alcohol, which was then allowed to evaporate. The resulting solid was then

lightly ground before use. It was found that the Mössbauer spectra of randomized samples were similar to the spectra of unrandomized samples if their particle size was below 5 μm E.S.D. Samples with particle sizes greater than three hundred mesh, 53 μm E.S.D., showed pronounced orientation effects in their spectra.

Instrumentation and technique. The samples were investigated using a 400-channel analyser operating in the multiscaler mode, coupled to a precision velocity generator described by Clark *et al.* (1967). The spectra were accumulated as mirror images in the first and second 200 channels of the analyser. The source used was 5 mC of ^{57}Co in a Pd matrix, having a halfwidth of 0·14 mm sec^{-1} measured against a thin potassium ferrocyanide absorber. The gamma rays were detected with a thin NaI(Tl) scintillator mounted on a photomultiplier tube.

In view of the low iron content of most of the samples and the low mass absorption coefficient of the constituent ions, no great attention was paid to sample thickness, it being merely ascertained that each sample transmitted greater than 50 % of the incident 14·4 keV radiation. The low iron content micas necessitated very long runs, in the order of a week to ten days, to obtain well-resolved spectra. All the experiments were performed at room temperature. Results were also obtained for the Lee Moor and Madagascar muscovites at 4·2 °K, but were not sufficiently different from the room temperature results to warrant inclusion in the tables.

Computer analysis of results. The Mössbauer spectra were fitted on an ICL 4-50 computer using a programme that employed the minimization procedure 'Flepomin' (Fletcher, 1966). This procedure is a modified 'steepest descent' method and is monotonically convergent. The mica spectra were initially fitted with two quadrupole doublets, one ferrous and one ferric, constrained so that the intensities and half-widths of the components of each doublet were kept equal. Three doublets were then fitted with the same constraints, and the final fit was obtained with all parameters varying independently.

χ^2 was used as a goodness of fit parameter. For a 200-channel spectrum and nineteen variables, χ^2 should be centred on 181, the number of degrees of freedom, but to be statistically acceptable should be less than about 230. Well resolved spectra and mirror-image-added spectra sometimes show values higher than this, probably due to higher resolution showing up errors in the fitted model. The most likely error is in the line shape, which has been assumed to be Lorentzian in all the fitting processes. Non-Lorentzian line shapes would be caused by the more remote environments of the iron atoms in each site not all being identical, giving rise to line broadening.

The first and second 200 channels were fitted separately, and then mirror-image added about the mean of the peak positions. The resulting spectrum was then fitted as before. The results given in table II are either the average of the results from the first and second 200 channels or the results of the mirror-image add, whichever seemed more satisfactory.

Muscovites. The structure of muscovite has been accurately determined by Rado-slovich (1960) and further refined by Veitch and Radoslovich (1963). A detailed

examination of the octahedral layer shows that there are two different octahedral sites, distinguishable by both size and symmetry. One site, that generally occupied by aluminium, has two hydroxyl groups on adjacent corners of the octahedron and an average anion–cation distance of 1·95 Å. The other site, that generally vacant, has the two hydroxyl groups on opposite corners of the octahedron and an average anion–cation distance of 2·20 Å. The ratio of the number of small sites to large sites is two to one.

TABLE II. *The isomer shift, quadrupole splitting, and halfwidth at half height are in mm sec^{-1}, with a maximum error of $\pm$0·02 mm sec^{-1}. The areas are expressed as fractions of the total absorption area, with a maximum error of $\pm$5 %. The errors are the standard deviations on the smallest peaks in the spectrum, generally the Fe''_B ions in the dioctahedral micas or the Fe''' ions in the trioctahedral micas, these being the least well-defined peaks. The errors on the other peaks are usually much smaller than quoted. The isomer shifts are given relative to sodium nitroprusside*

	χ^2	Fe_A^{2+}				Fe_B^{2+}				Fe^{3+}			
		I.S.	Q.S.	H.W.	Area	I.S.	Q.S.	H.W.	Area	I.S.	Q.S.	H.W.	Area
1	179	1·41	3·02	0·16	0·43	1·39	2·25	0·27	0·11	0·60	0·82	0·39	0·47
2	179	1·41	3·04	0·17	0·23	1·36	2·14	0·26	0·05	0·63	0·74	0·33	0·72
3	267	1·41	3·08	0·21	0·28	1·41	2·20	0·25	0·11	0·61	0·79	0·38	0·62
4	190	1·40	2·90	0·23	0·27	1·36	2·28	0·30	0·37	0·66	0·81	0·38	0·36
5	195	1·36	2·56	0·17	0·56	1·34	2·24	0·21	0·34	0·73	0·80	0·22	0·10
6	214	1·33	2·58	0·15	0·46	1·32	2·14	0·20	0·37	0·65	0·72	0·23	0·19
7	218	1·38	2·61	0·16	0·43	1·37	2·19	0·23	0·33	0·66	0·82	0·34	0·25
8	181	1·39	2·74	0·12	0·20	1·39	2·44	0·19	0·70	0·64	0·83	0·24	0·11
9	229	1·41	2·65	0·23	0·84	—	—	—	—	0·66	0·89	0·26	0·17
10	290	1·42	2·96	0·17	0·52	—	—	—	—	0·57	—	0·97	0·48
11	164	—	—	—	—	—	—	—	—	0·63	0·57	0·23	1·00
12	192	1·39	2·60	0·14	1·00	—	—	—	—	—	—	—	—

1. Lee Moor muscovite.	2. Madagascar muscovite.	3. M2
4. M1	5. Indian phlogopite.	6. Aberdeen biotite.
7. Tregarden biotite.	8. Trelavour biotite.	9. Zinnwaldite
10. Gilbertite.	11. Pyrophyllite.	12. Talc.

In view of the difference in the site sizes in the octahedral layer, it has been suggested (Veitch and Radoslovich, 1963) that octahedral ordering should occur, the small trivalent ions such as aluminium and ferric iron occupying the smaller site, and the larger divalent ions such as ferrous iron and magnesium occupying the larger site. It would appear that the evidence supporting this theory is not extensive.

As can be seen from table II and fig. 1, the Mössbauer spectrum of a typical muscovite can be resolved into three quadrupole doublets, two with parameters characteristic of octahedral ferrous iron and one characteristic of octahedral ferric iron. The two ferrous doublets have markedly different quadrupole splittings and areas, the inner doublet being in general much less intense than the outer doublet.

Ingalls (1964) has shown that for ferrous iron in an octahedral site the quadrupole

splitting decreases with increasing distortion of the site from octahedral symmetry. On this basis one would expect ferrous iron in the smaller, less symmetric octahedral site in muscovite to have the smaller quadrupole splitting, and the inner ferrous doublet is assigned to this site accordingly. Thus it can be seen that in general the ferrous iron tends to occupy the larger, more symmetric site, confirming the theory quoted above. The occupation of this site is not exclusive in any of the muscovites studied, although in the Madagascar muscovite the iron in the smaller site was only just resolved. In the
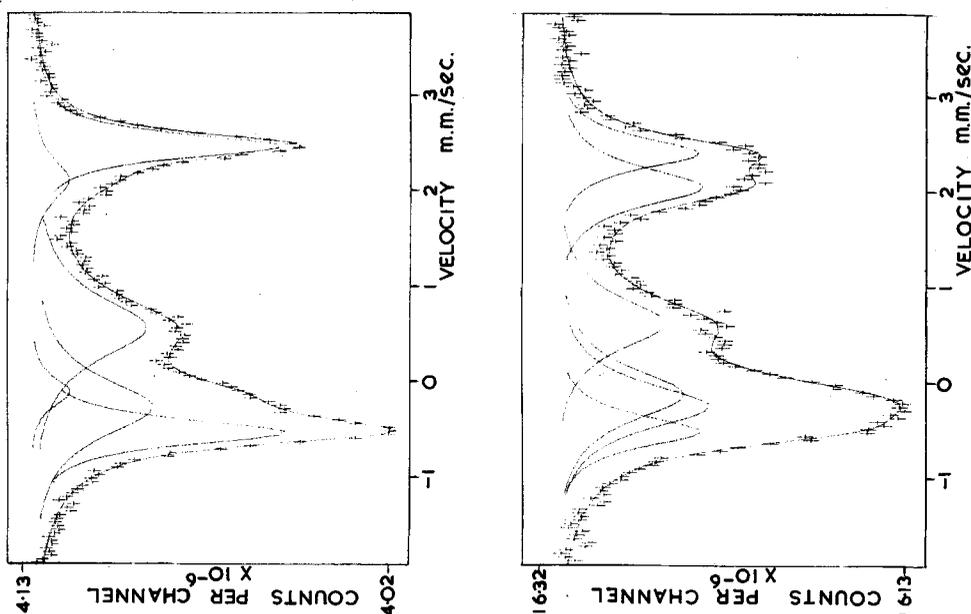
FIGS. 1 and 2: Fig. 1 (left). The Mössbauer spectrum of a typical dioctahedral mica, Lee Moor muscovite. Fig. 2 (right). The Mössbauer spectrum of mica M1.

mica M1 (fig. 2) the ferrous iron is more evenly distributed between the two sites, but allowing for the ratio of site numbers there is still a preference for the larger site. The increased amount of ferrous iron in the smaller site of this mica may be related to its higher MgO content, which may influence the structure of the mica, or the magnesium may tend to occupy the larger octahedral site in preference to ferrous iron.

The halfwidths of the peaks in the ferric doublet are considerably broader than those of the ferrous peaks and broader than those published for ferric iron in other minerals (Bancroft *et al.*, 1968). This suggests that there are two unresolved ferric doublets present, due to ferric iron in both octahedral sites.

Phlogopite and biotite. The structure of phlogopite has been accurately determined by Donnay (1964) and is similar in basic respects to that of muscovite except that all the octahedral site sizes are virtually the same, the average anion–cation distance being 2·106 Å for both types of site. Hence the two sites can only be distinguished on

the basis of symmetry and one would not expect any appreciable octahedral ordering.

The spectrum of a typical trioctahedral mica is shown in fig. 3. From this and from table II it can be seen that the spectra can be resolved into three quadrupole doublets, two ferrous and one ferric, as in the case of the muscovites. By a parallel argument to that used for the muscovite spectra, the inner ferrous doublet is ascribed to the octa-hedral site with the two hydroxyls adjacent, and the outer doublet to the site with the
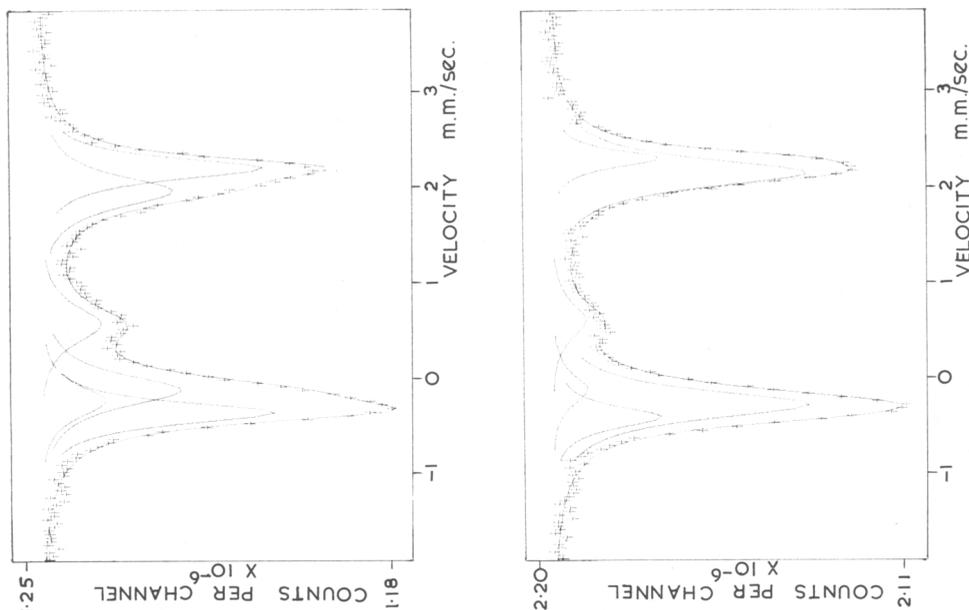
FIGS. 3 and 4: Fig. 3 (left). The Mössbauer spectrum of a typical trioctahedral mica, Aberdeen biotite. Fig. 4 (right). The Mössbauer spectrum of the Trelavour biotite.

two hydroxyls opposite. The difference between the ferrous quadrupole splittings in the dioctahedral micas is larger than that for the trioctahedral micas, due to the difference in site sizes between the two types of mica. The quadrupole splitting of the outer ferrous doublet in muscovites is larger than that for trioctahedral micas. However, there is little difference in the quadrupole splittings of the inner ferrous doublets, in spite of there being a greater difference in the relevant site sizes. This would suggest that the asymmetric site in trioctahedral micas is more distorted than that in muscovites.

From the relative areas of the two ferrous doublets it can be seen that there is some preferential occupation of the more symmetric site. The ordering is not as pronounced as in muscovite, but allowing for the ratio of site numbers amounts to at least a two to one preference for the more symmetric site. There is no obvious explanation for this ordering.

No great amount of information can be obtained from the ferric doublets in these

micas. The isomer shifts and quadrupole splittings are similar to those obtained for most of the muscovites and are typical of octahedral ferric iron. Taylor *et al.* (1968) claim to have resolved both octahedral and tetrahedral ferric iron in the Mössbauer spectrum of a biotite, but if this claim is based on their published spectra, which have few points and poor resolution, then it cannot be taken seriously. The halfwidths of the ferric peaks are smaller than in the muscovites. In the muscovites it was suggested that ferric iron occupies both octahedral sites, producing two unresolved ferric doublets. It seems reasonable to think that a similar situation exists in trioctahedral micas, but due to the similarity in the site sizes the two ferric doublets are virtually superimposed, giving no line broadening.

The parameters of the spectrum of the Trelavour biotite (fig. 4) were very different from those obtained for other trioctahedral micas. A possible explanation for this difference may be found in the composition; the mica contains $1 \cdot 5$ % Li_2O. The presence of the lithium may alter the dimensions of the octahedral layer so that it becomes more like a zinnwaldite, and further mention of this mica will be made under the zinnwaldite heading.

Zinnwaldite. The structure of zinnwaldite is less accurately known than the structures of muscovite and phlogopite. Rieder (1968) has proposed a structure based on chemical and crystallographic evidence in which the octahedral sites are ordered into large and small sites, the large sites being those with hydroxyls adjacent, and the small sites being those with hydroxyls opposite. On this basis one would expect the Mössbauer spectrum to show two ferrous quadrupole doublets with similar isomer shifts, but different quadrupole splittings and intensities. The more intense doublet should have a quadrupole splitting similar to those found in biotites, the less intense doublet should have a splitting somewhat larger than this.

The spectrum of the zinnwaldite could only be resolved into two doublets, one ferrous and one ferric. The quadrupole splitting of the ferrous doublet is larger than generally found in other trioctahedral micas but is closer to them than to the values obtained for muscovites. The linewidths of this doublet are broader than in other trioctahedral micas suggesting the presence of two unresolvable doublets. The value of the quadrupole splitting neither supports nor opposes Rieder's suggested structure, as ferrous iron in either octahedron could produce such a value. The quadrupole splitting of the ferric doublet on the other hand is considerably larger than in any of the other micas. This would suggest that at least one of the octahedral sites is considerably more distorted from octahedral symmetry than in any other mica examined, and one would not expect this from the structure proposed by Rieder.

Herzenberg *et al.* (1968) have obtained the Mössbauer spectrum of a zinnwaldite from South Dakota. Their value for the ferrous quadrupole splitting, $3 \cdot 13 \pm 0 \cdot 05$ mm sec^{-1}, is larger than any room temperature value observed in this study. They also note that the ferric doublet, although poorly resolved, appears to have a quadrupole splitting smaller than in any micas previously studied. These two points conflict directly with the corresponding points in this study, and suggest that there are considerable differences between the two samples.

It is interesting to note that the spectrum of the lithium-rich Trelavour biotite discussed in the previous section is just what one would expect from a mica having the structure proposed by Rieder. The X-ray diffraction pattern of this mica is not well defined: the only peaks visible in the lower orders are basal peaks, but the higher order reflections suggest that the mica is a biotite. The chemical analysis also favours a biotite, there being less silica and more ferrous iron than found in zinnwaldites. Thus the evidence regarding the structure of this mica is conflicting, but in view of the rather poor X-ray pattern we feel that it is quite possible the Trelavour biotite has a structure similar to that proposed by Rieder for zinnwaldites.

Gilbertite is a secondary dioctahedral mica resembling muscovite. The Mössbauer spectrum of gilbertite agrees with this, although it is very poorly resolved, due to the low iron content. The quadrupole splitting and isomer shift of the ferrous doublet correspond fairly well with the outer doublet of muscovite. The ferric doublet in gilbertite was not resolvable into anything other than a broad single line, with rather a low isomer shift relative to the other muscovites, but not necessarily in the range of tetrahedral ferric iron.

Pyrophyllite and talc. The Mössbauer spectrum of pyrophyllite shows a single ferric quadrupole doublet with an isomer shift similar to the ferric doublet found in muscovites, but with a smaller quadrupole splitting and peak halfwidth. The smaller halfwidth suggests that only one of the two available octahedral sites is occupied by ferric iron, unlike the muscovite situation. This site is presumably the smaller, less symmetric of the two, as this is the site occupied by trivalent ions in the ideal structure. If this is so, then the larger quadrupole splitting of the ferric doublet in muscovites relative to that in pyrophyllite is a reflection of the distortion of the octahedral layer in muscovites due to the presence of interlayer potassium (Veitch and Radoslovich, 1963).

The spectrum of talc shows a single ferrous doublet with isomer shift and quadrupole splitting comparable with the outer ferrous doublet of phlogopite. This suggests first that the ferrous iron in talc occupies the more symmetric octahedral site and second that the presence of interlayer potassium in trioctahedral micas does not distort the octahedral layer significantly.

The *ferrous:ferric ratios* as measured from the Mössbauer spectra do not always agree with those determined chemically:

$\frac{FeO}{Fe_2O_3}$		1	2	3	4	5	6	8	10
	Chemical	0·47	0·25	0·45	0·48	10·0	3·4	8·2	0·51
	Mössbauer	1·00	0·35	0·57	1·60	8·1	3·9	8·1	0·97

In particular, the muscovites tend to show more ferrous iron in the Mössbauer results than in the chemical analyses. A similar trend is seen in the results of Bowen *et al.* (1969). There are two possible reasons for this: first, the recoilless fractions of ferrous and ferric iron may not be the same. If this is the case, one could expect a considerable variation in the ferrous:ferric ratio with temperature. No such variation was seen in either the Lee Moor or Madagascar muscovites even when cooled to 4·2 °K. The

second possible explanation is that there has been some oxidation on chemical analysis. The methods of analysis used were fairly standard. Micas M1 and M2 were dissolved in H_2SO_4/HF under an inert atmosphere, the solution treated with boric acid to complex fluoride, and the ferrous iron determined by titration with dichromate. The other micas were dissolved similarly and the ferrous iron determined colorimetrically with dipyridyl. The results obtained by these methods are claimed to be reproducible to within 5 %, giving a reproducibility on the ferrous:ferric ratio of ± 7 %. A similar figure is claimed for the accuracy of the Mössbauer values. Thus there are discrepancies outside the claimed experimental errors. In view of the acknowledged difficulty in measuring ferrous iron by chemical means, we feel that the Mössbauer results are probably more reliable, and that Mössbauer spectroscopy provides a better method for determining ferrous iron in minerals than chemical analysis.

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