

Polarized optical absorption and ^{57}Fe Mössbauer study of pegmatitic muscovite

JAMES FINCH, A. ROSS GAINSFORD AND W. CRAIGHEAD TENNANT

Chemistry Division
Department of Scientific and Industrial Research
Private Bag, Petone, New Zealand

Abstract

^{57}Fe Mössbauer spectra and polarized absorption spectra in the region 4000–6800Å are reported for 14 common pegmatitic muscovites, 12 of which were selected from an extensive pegmatite complex. They were chosen to cover a wide range of color types (deep green, green, red-green and ruby-red) and ferric/ferrous ion ratios. Optical absorption properties are discussed in terms of the Fe^{2+} , Fe^{3+} distribution in the M1 and M2 sites. Background absorption, and hence depth of color, appears to be determined primarily by an intense metal-ligand charge transfer which peaks in the UV and the intensity of which correlates linearly with the Fe^{2+} concentration in the normally unoccupied M2 site. The presence or absence of the Fe^{2+} – Fe^{3+} metal-metal charge transfer bands in the region 5000–6000Å gives rise to the red and green hues observed in the muscovites studied.

Introduction

There have been a number of Mössbauer studies of iron distribution within micas in general (*e.g.*, Bowen *et al.* 1969; Hogg and Meads, 1975; Goodman 1976) and also a number of studies of optical absorption in muscovite, lepidolite and related minerals (*e.g.*, Finch, 1963; Ruthberg *et al.*, 1963; Faye, 1968a, b; Robbins and Strens, 1972). However, there have been only limited attempts to relate Mössbauer spectra to absorption spectra in micas (Richardson, 1975, 1976; Marfunin *et al.*, 1969). Of these, only that by Richardson dealt with muscovite and it was the uncommon rose variety. This study is an attempt to correlate Mössbauer parameters with absorption characteristics in a more ubiquitous variety of muscovite.

Those muscovites variously described as pale green, ruby, buff, yellowish, greenish-brown and reddish-brown are by far the most common and are colored to a major extent by iron in one or both of its +2 and +3 oxidation states. Those described as emerald green, olive green, pink (rose), gray and blue are rare and the extent to which these colors are due to one or more of the possible chromophores Fe, Mn, Ti, V and Cr is not always certain. The aim then was to limit the study to closely spaced members of a coherent compositional and structural group containing iron as the most likely

chromophore and containing only a limited range of colors. In particular it was desirable to choose a single polymorphic form of muscovite (the $2M_1$ polymorph) and select material which was free of such complicating factors as inclusions, cracks, distortion patterns and growth phases that are frequently associated with observable color zones. Therefore, pegmatitic muscovites which contained areas free from any of these irregularities and in which there was the least likelihood of absorption being influenced by Mn, Ti, V and Cr were chosen. By this means, the number of peripheral parameters liable to effect absorption were minimized.

One of us (Finch, 1963) had earlier selected specimens on the above basis from an extensive pegmatite complex in the Harts Range, Australia, and indicated by polarized absorption studies that there could be as many as five mutually independent curve characteristics. Accompanying optical crystallographic studies suggested the probability of structural factors being involved. Also, by careful selection of specimens, similar absorption results were obtained by Ruthberg *et al.* (1963) for seven muscovites, of varying colors, from widely different world sources. From their work of correlating non-polarized absorption features, apparent 2V and color, they obtained three basic spectral types which they related to chemical and structural variations.

Having established iron as the most probable chromophore in the samples, the principal aim of the present work was to see if the distribution of Fe^{2+} and Fe^{3+} in the M1, M2 sites, as determined by Mössbauer spectroscopy, could be related to the absorption characteristics. All the selected muscovites exhibited considerable pleochroism in the basal plane and a secondary aim sought relations between this pleochroism and iron distribution. In a subsequent study we shall present single crystal Mössbauer results on a selection of the present muscovites from the high ferrous and high ferric ends of the series.

Determinative procedures

Sample preparation

Pieces of the selected muscovites (mainly from the Australian Harts Range collection, Finch, 1963) required for absorption spectra were cut from sheets 0.2–0.4 mm thick to give plates with 20–30 mm edges parallel to the *a* and *b* crystallographic axes. Each such plate was selected from the approximate center of a larger area having no color or other discernable changes. Material for Mössbauer and composition studies consisted of flakes cleaved from these plates and sample material adjacent to them. The analytical solutions and the buttons for XRF analyses were prepared from this flake material by borate fusion methods.

Powders for the Mössbauer studies were prepared by grinding the flake material for 55–60 seconds in a tungsten carbide swing mill, floating off the fine fractions from a suspension in methyl alcohol and evaporating this float material to dryness. (Microscopic examination showed the particle size to be $<0.5 \mu\text{m}$.) In order to check that this method of sample preparation did not alter the muscovite, powders were also prepared by collecting the drillings from a sheet of one of the muscovite samples while using a slowly revolving tungsten carbide burr. Indistinguishable X-ray and Mössbauer spectra were obtained from samples prepared by these two methods.

Chemical composition. Total iron was determined spectrophotometrically and the borate solutions were then used for atomic absorption determinations of Si, Al, Ca, Mg, Na, K, Ti, Mn, V and Cr and to confirm the Fe determinations. Further analyses by XRF were carried out on a few selected, but widely representative, samples to check and supplement the spectrophotometric and atomic ab-

sorption analyses. All of the analytical results are summarized in Table 1.

Polarized absorption spectra. Absorption spectra for each of the *Y* and *Z* vibration directions were initially determined with a double beam recording spectrophotometer in which both exit beams were polarized by a polaroid sheet set against the base plate of the exit windows. As the polarized components of the reference and sample beams were not identical before they reached the polarizing filter, this gave an undulating base line. A correction, in effect giving a straight base line, had therefore to be applied at specific wavelengths (20Å intervals) throughout the region scanned. These appropriate corrections were calculated by reference to one wavelength at which the polarized differential between the two beams was zero.

Absorption measurements were taken from the recorded curves (at these 20Å intervals), corrected for baseline undulation as described above, corrected for reflection losses and finally converted to absorbances for a standard thickness of 0.381 mm. These corrected measurements were then plotted logarithmically against wavelength to give λ vs. $\log A$ curves, where *A* is the corrected absorbance. This method of presenting the spectra allows direct and simple comparison of absorption features such as hue, pleochroism and peak intensities.

Mössbauer spectra. Mössbauer spectra of about 200 mg (2–5 mg Fe/cm^2) of the powders were measured on a constant acceleration Mössbauer spectrometer utilizing a Harwell velocity transducer. Spectra were stored as mirror images in the two halves of the 1024 channel memory of an ORTEC Model 6240A multi-channel analyzer. The source used was 5 mC $^{57}\text{Co}/\text{Pd}$. Isomer shifts were measured with respect to an iron foil (99.999% purity). The number of counts per channel accumulated varied between 10^6 and 10^7 for each spectrum. All spectra were recorded at room temperature.

The mirror image spectra were fitted to Lorentzian line shapes, the program and method used being similar to that of Bancroft (1973). The spectra were all fitted with quadrupole doublets, two ferrous and one ferric (three doublets) and two ferrous and two ferric (four doublets) constrained so that the intensities and half-widths of the components of each doublet were kept equal. All ferrous half-widths were constrained to be equal, but allowed to be different from the ferric half-widths. In the four doublet fit, all ferric half-widths were constrained to be equal.

Table 1. Analytical results

	PG2	MG10	JFAL	MG1	SP/LTB	DG2	BG4	SG-SR/7A	SG-SR/2A	SG-SR/6A	R1	VLS/G	WD	"Ideal"
SiO ₂	45.45 ^A	45.4	45.4	45.81 ^A	45.9	45.9	45.84 ^A	45.7	45.9	45.4	45.6	45.58 ^A	46.29 ^A	45.25
Al ₂ O ₃	34.02	32.1	33.1	34.29	35.3	31.9	31.68	35.2	34.9	35.1	34.6	35.36	34.50	38.40
K ₂ O	10.91	11.00	10.54	10.78	10.24	10.92	10.76	10.64	10.74	10.64	10.87	10.58	10.92	11.83
Na ₂ O	0.74	0.59	0.61	0.28	1.21	0.54	0.46	0.75	0.77	0.78	0.67	0.72	0.84	
CaO	0.10	0.10	0.08	0.10	0.08	0.10	0.10	0.08	0.10	0.10	0.10	0.10	0.10	
Fe ₂ O ₃ ^B	3.79	5.05	3.95	3.44	2.63	4.41	4.49	2.43	2.44	2.37	2.31	2.15	1.86	-
FeO ^B	0.49	0.80	0.69	0.74	0.71	1.36	1.41	1.02	1.09	1.09	1.11	1.20	1.14	-
Ti ₂ O ₂	0.16	0.28	0.22	0.07	0.10	0.53	0.18	0.08	0.23	0.12	0.32	0.04	0.19	
Mn ₂ O ₃	0.13	0.06	0.07	0.03	0.04	0.06	0.11	0.06	0.04	0.05	0.05	0.06	0.01	-
MgO	0.58	1.04	0.83	0.74	0.93	1.54	0.52	0.20	0.89	0.36	1.03	0.10	0.85	
H ₂ O	4.36 ^C	(4.52)	(4.52)	4.48 ^C	(4.52)	(4.52)	4.62 ^C	(4.52)	(4.52)	(4.52)	(4.52)	4.59 ^C	4.60 ^C	4.52
Total ^D	100.73	100.94	100.01	100.76	101.66	101.78	100.17	100.72	101.62	100.53	101.18	100.48	101.30	100.00

A. Analytical results determined by XRF; results for all other muscovite samples were determined by atomic absorption, spectrophotometrically and emission spectrograph.

B. Distribution of iron as Fe³⁺ and Fe²⁺ from Mössbauer parameters.

C. Results as loss on ignition in preparation of samples for XRF analyses; water content of all other muscovite samples was assumed to be that of the ideal formula.

D. Vanadium and chromium contents were less than 0.01% for all the samples.

Results

Table 2 summarizes the Mössbauer parameters of the fourteen muscovites studied. For convenience, the results are tabulated in descending order of Fe³⁺/Fe²⁺ ratios. Column 2 of the table lists the

colors of the muscovite sheets based on the color classification suggested by Finch (1963). Typical room temperature Mössbauer spectra of four selected muscovites, covering a wide range of Fe³⁺/Fe²⁺ ratios, are given in Figure 1. Goodman (1976) has been followed regarding assignment of ferrous ions

Table 2. Mössbauer parameters and colors (293K)

Name	Color #	Total Fe (%) [*]	Fe ³⁺ /Fe ²⁺ †	% total iron as:			Fe ²⁺ (M1)			Fe ²⁺ (M2)			Fe ³⁺ (M1)			χ ²
				Fe ²⁺ (M1)	Fe ²⁺ (M2)	Fe ³⁺ (M1)	I.S.	Q.S.	H.W.	I.S.	Q.S.	H.W.	I.S.	Q.S.	H.W.	
							mm s ⁻¹			mm s ⁻¹			mm s ⁻¹			
PG2	1	3.03	6.87	7.9	4.8	87.3	1.21	2.99	0.44	1.14	2.12	0.44	0.36	0.86	0.96	1021
MG10 Area A	2	4.16	5.71	6.9	8.0	85.1	1.16	3.06	0.47	1.13	2.18	0.47	0.38	0.86	0.95	1122
JFAL	1	3.30	4.71	12.8	4.7	82.5	1.16	2.97	0.49	1.15	2.12	0.49	0.34	0.82	0.94	1073
MG1	2	2.98	4.10	12.9	6.7	80.4	1.21	2.98	0.50	1.16	2.09	0.50	0.37	0.84	1.19	1071
SP/LTB	3	2.39	3.35	11.7	11.3	77.0	1.20	2.97	0.41	1.12	2.10	0.41	0.35	0.83	1.24	1057
DG2	4	4.15	2.92	13.8	11.7	74.5	1.19	2.96	0.48	1.13	2.19	0.48	0.38	0.81	1.03	1109
BG4	5	4.23	2.88	19.8	6.0	74.2	1.16	2.97	0.50	1.09	2.10	0.50	0.37	0.83	1.01	1115
SG-SR/7A	6	2.50	2.14	23.2	8.6	68.2	1.19	3.05	0.44	1.13	2.12	0.44	0.37	0.86	1.10	1061
SG/SR/2A	7	2.56	2.01	18.2	15.0	66.8	1.19	3.01	0.49	1.14	2.14	0.49	0.37	0.84	1.08	1000
SG-SR/6A	6	2.50	1.95	24.3	9.6	66.1	1.17	3.05	0.48	1.16	2.14	0.48	0.37	0.87	1.19	1008
R1	3	2.48	1.88	20.1	14.6	65.3	1.19	2.98	0.49	1.13	2.11	0.49	0.39	0.84	1.14	1101
VLS/G	7	2.44	1.60	28.8	9.6	61.6	1.18	3.06	0.48	1.10	2.09	0.48	0.38	0.80	1.22	1013
WD	8	2.19	1.47	22.5	18.0	59.5	1.20	2.96	0.44	1.16	2.09	0.44	0.39	0.82	0.96	1038
IRMP2/52 †	9	~2	0.85	35.5	18.7	45.9	1.21	2.97	0.40	1.19	2.11	0.40	0.36	0.83	1.01	1104

Visual description of color;

1 = pure green, 2 = greenish-brown, 3 = reddish, 4 = dark greenish-brown, 5 = bluish-green, 6 = reddish-green, 7 = greenish-red, 8 = red, 9 = Indian ruby.

* Obtained from replicate chemical analyses and confirmed by XRF and AA analyses on some selected specimens.

† Obtained from Mössbauer parameters. Errors in I.S. and Q.S. are ± 0.03 mm s⁻¹. The I.S. values are quoted relative to iron metal at room temperature.

‡ An obviously ruby-red specimen not available at a later date for further study but included here to show continuing trends of Mössbauer parameters.

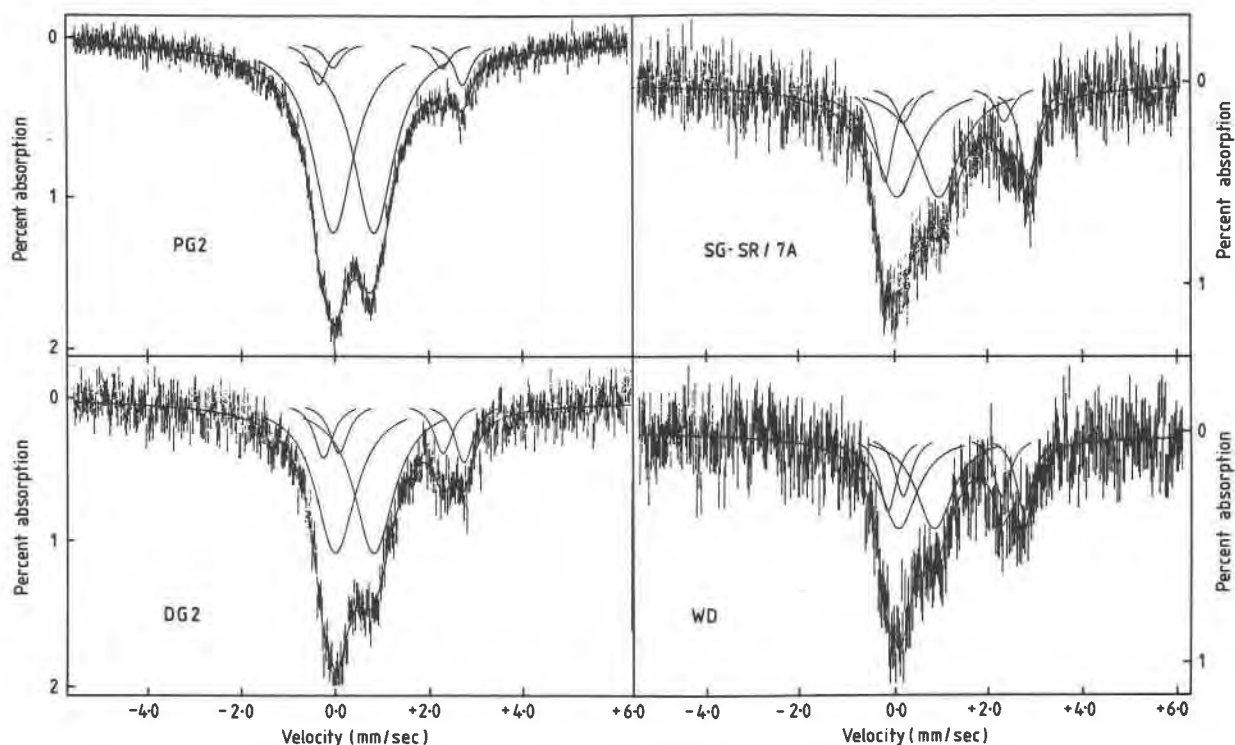


Fig. 1 Typical room temperature Mössbauer powder spectra of four selected muscovites. Velocities shown are taken relative to a metallic iron standard absorber.

and site nomenclature; Fe^{2+} with the larger quadrupole splitting is assigned to the smaller cis-hydroxyl M1 site and the Fe^{2+} with the smaller splitting to the larger, normally unoccupied, trans-hydroxyl M2 site.

Chemical formulae based on analytical results (Table 1) and the Mössbauer results are given in Table 3. Polarized absorption spectra (4000–6800Å) for the above four muscovites are shown in Figure 2.

Discussion

The names used in this study to describe colors are not necessarily the same as those used by Ruthberg *et al.* (1963) but the range of colors (hues) and the accompanying absorption peaks in both instances are very similar.

It is important to note that the 'red' muscovites in this work are not to be confused with the so-called red ferrian muscovite from Sogn, Norway, reported

Table 3. Chemical formulae—muscovite micas

Name	(K ⁺)	(Na ⁺)	(Ca ²⁺)	(Fe ³⁺ (M1))	(Fe ²⁺ (M1))	(Fe ²⁺ (M2))	Al ³⁺	Ti ³⁺	Mg ²⁺	Mn ³⁺	(Si ⁴⁺)	Al ³⁺	(O ²⁻)	(O ²⁻ -H ⁺)	Excess*	
PG2	0.931	0.096	0.007	0.191	0.017	0.010	1.724	0.008	0.058	0.006	3.041	0.959	10.0	2.00	1.946	+0.014
MG1	0.916	0.036	0.007	0.172	0.027	0.014	1.742	0.003	0.074	0.002	3.051	0.949	10.00	2.00	1.988	+0.034
BG4	0.926	0.060	0.007	0.228	0.061	0.018	1.610	0.009	0.052	0.006	3.092	0.908	10.00	2.00	2.078	-0.016
VLS/G	0.899	0.093	0.007	0.108	0.050	0.017	1.810	0.002	0.010	0.002	3.035	0.965	10.00	2.00	2.038	-0.001
WD	0.921	0.108	0.007	0.279	0.035	0.028	1.751	0.010	0.084	0.001	3.062	0.938	10.00	2.00	2.029	+0.002
IDEAL	1.000						2.000				4.000		10.00	2.00	2.00	0.000

* Excess atoms in the octahedral layer.

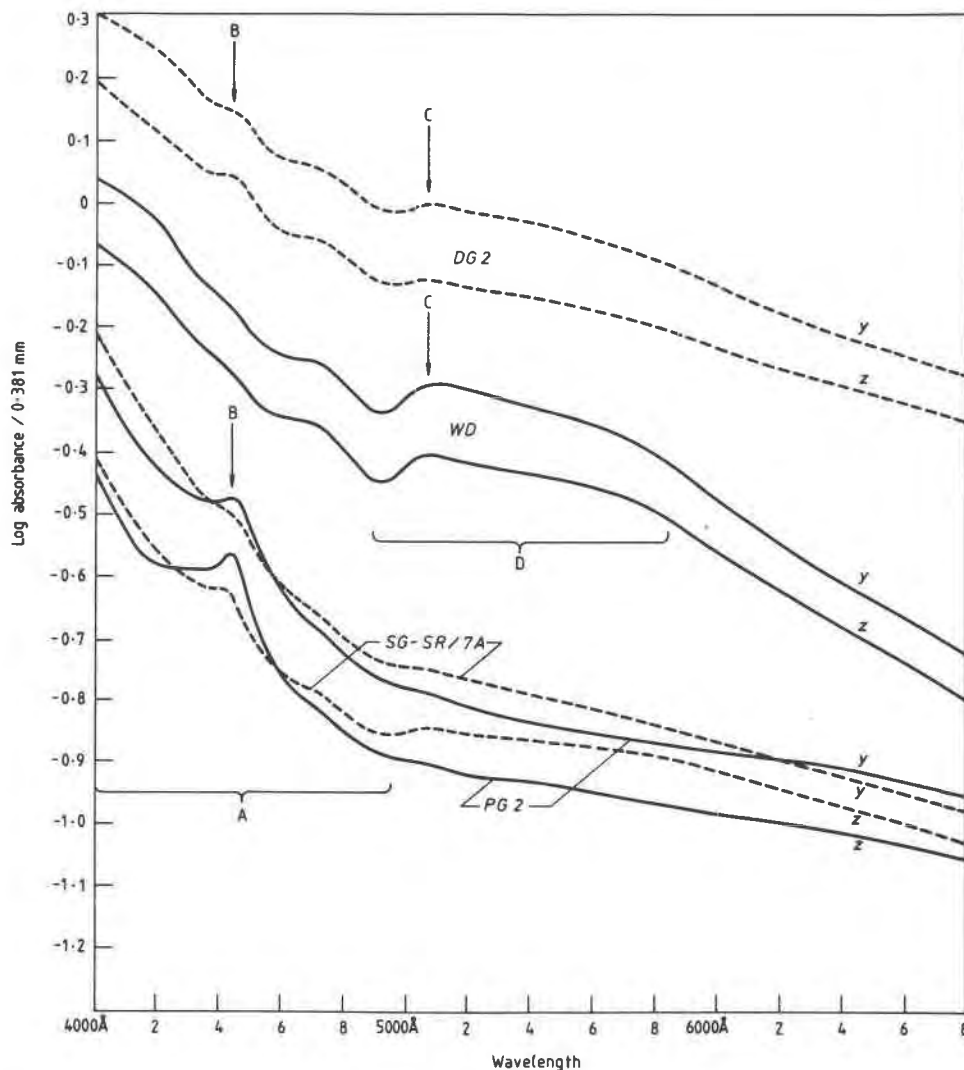


Fig. 2 Optical absorption spectra (λ -log absorbance curves) for the two principal vibration directions in the basal plane of the four selected muscovites in Fig. 1.

by Askvik (1972) and later studied by Mössbauer spectroscopy by Goodman (1976); this sample is in fact a 'rose' muscovite in which the color probably arises (Askvik, 1972) from Mn^{3+} (the Mn_2O_3 content is given as 0.87%). The muscovites in the present work contain no more than 0.13% Mn_2O_3 , the highest being in the 'pure green' sample PG2 and the bluish-green sample BG4. It is clear, then, that Mn does not contribute significantly to the colors of the muscovites studied. Apart from this, the significant differences in Mn contents of the samples could not be correlated with any of the absorption features. Specimens were also chosen with the hope of being able to disregard any influence due to vanadium and chromium. It is most

unlikely from the analytical results for these two elements (<0.01% in all the specimens) that either of them have contributed to any of the absorption features observed in these muscovites.

From Table 2, the color correlates approximately with the Fe^{3+}/Fe^{2+} ratios; the "pure green" (Finch, 1963) muscovites are those with the highest ferric iron and the "reds" are those with the highest ferrous iron concentrations. Inasmuch as this shows a basic chemical variation related to color, a similar observation for their series was made by Ruthberg *et al.* (1963). As discussed below, the overall absorption in the visible region is strongly influenced by an intense UV band which "tails" into the visible region. Observed colors, or hues,

depend only to a minor extent on the tail of this absorption, being largely controlled by the spectral response curve of the human eye which peaks in the green-yellow region of the spectrum. Consequently, factors controlling absorption in the 4900–5800Å region are crucial to any discussion on colors in muscovite.

Absorption of visible light in dioctahedral and trioctahedral micas is then (Robbins and Strens 1972, Smith and Strens, 1976, Kliem and Lehmann, 1979) a function of the intense absorption band which peaks in the UV and "tails" into the visible (region A, Fig. 2), together with several weaker bands in the visible region. These latter are variously described as intervalance charge transfer (Smith and Strens, 1976), ferric iron clusters (Kliem and Lehmann, 1979) and Fe^{3+} ligand field transitions (Faye, 1968a), and determine the observed colors. For a series of biotites, Robbins and Strens (1972) assigned the intense band in the UV to a metal-ligand ($\text{Fe}^{2+} \rightarrow \text{O}$) charge transfer band and showed a linear relation between absorbance at 5900Å and FeO content. For a different group of biotites, Kliem and Lehmann (1979) on the other hand, present good evidence for regarding the band in the UV as being an absorbance due to ferric iron clusters. These two options in the case of muscovites are dealt with later in the discussion but first, the distribution of Fe^{2+} and Fe^{3+} in the M1 and M2 sites of the muscovites studied must be examined.

It was assumed, following Bancroft and Brown (1975), that the experimentally determined Mössbauer peak areas could be used quantitatively to assign ferrous and ferric iron to the appropriate sites. The distribution of Fe^{2+} and Fe^{3+} in the M1 and M2 sites is then shown in Table 2.

Fe^{3+} has been assigned to the M1 site only. However, there is some doubt as to the distribution of Fe^{3+} in the sites of the octahedral and tetrahedral layers. For every sample, we have tried to refine 8 peaks, assuming two ferric doublets, but in no case have we been able to obtain parameters which are realistic and for which χ^2 was less than that for a 6 peak fit, assuming one ferric doublet. This could be taken to indicate, in agreement with Goodman's (1976) results for the Sogn ferrian (rose) muscovite, that ferric ion enters only the M1 site, even though the half-widths of the Fe^{3+} peaks are about twice that of the Fe^{2+} peaks (see Table 2). As half-widths of this magnitude obtained for Fe^{3+} are strongly indicative of multiple site occupancy, there remains the possibility, unproven, that Fe^{3+} enters both the

M1 and M2 sites and may also occupy the tetrahedral sites in the mica structure although, as noted above, we have found no direct evidence for this. There is also the possibility that the relatively wide half-widths for both Fe^{2+} and Fe^{3+} are due to disorder in the occupancy by iron in the sites and the influence of the next neighbor as described in pyroxenes (Dowty and Lindsley, 1973) and omphacites (Aldridge *et al.*, 1978).

Fe^{2+} was found in both the M1 and M2 sites (Table 2) in all the muscovites studied, with the M2 occupancy normally less than that of M1 and never significantly greater. Goodman (1976) has suggested that the M2 site in dioctahedral micas is only occupied when the M1 site is filled, with Al^{3+} in the ideal structure, but with varying amounts of divalent and trivalent replacement cations such as Fe^{3+} , Fe^{2+} , Ti^{3+} , Mg^{2+} and Mn^{3+} in most natural micas. There appears to be no adequate way of checking this proposal but, assuming it is correct, Mössbauer assignments and chemical formula calculations for the five muscovites of this study for which precise analytical data were available, indicate (Table 3) that the only significant occupancy of M2 which can be established is by Fe^{2+} . We find this inference somewhat surprising and, in particular, there remains the strong possibility, as discussed above, that Fe^{3+} also occupies the M2 site.

Following earlier studies of biotites (Robbins and Strens, 1972, Kliem and Lehmann, 1979) the relationship between background absorbance and iron distribution in the muscovites was examined. There was no evidence of correlation between total Fe^{2+} and absorbance in region A (Fig. 1) as found for a series of biotites by Robbins and Strens. Nor could absorbance be correlated with Fe^{3+} content, a circumstance which might occur if, as suggested by Kliem and Lehmann for three biotites, the absorption band arises from clusters of Fe^{3+} ions. It is possible, of course, that the absorbance may depend on the extent of clustering rather than simply being related to total Fe^{3+} concentrations. However, as discussed below, it is reasonable to reject the Fe^{3+} cluster proposal apart from it making only a minor contribution to the background absorption.

In Figure 3(a) absorbance at 5150Å is plotted against percentage, by weight, of iron as Fe^{2+} in the normally unoccupied M2 site; a reasonable correlation is apparent. Figure 3(b) reveals better defined relationships between absorbance and this Fe^{2+} for the green muscovites in one grouping and the red

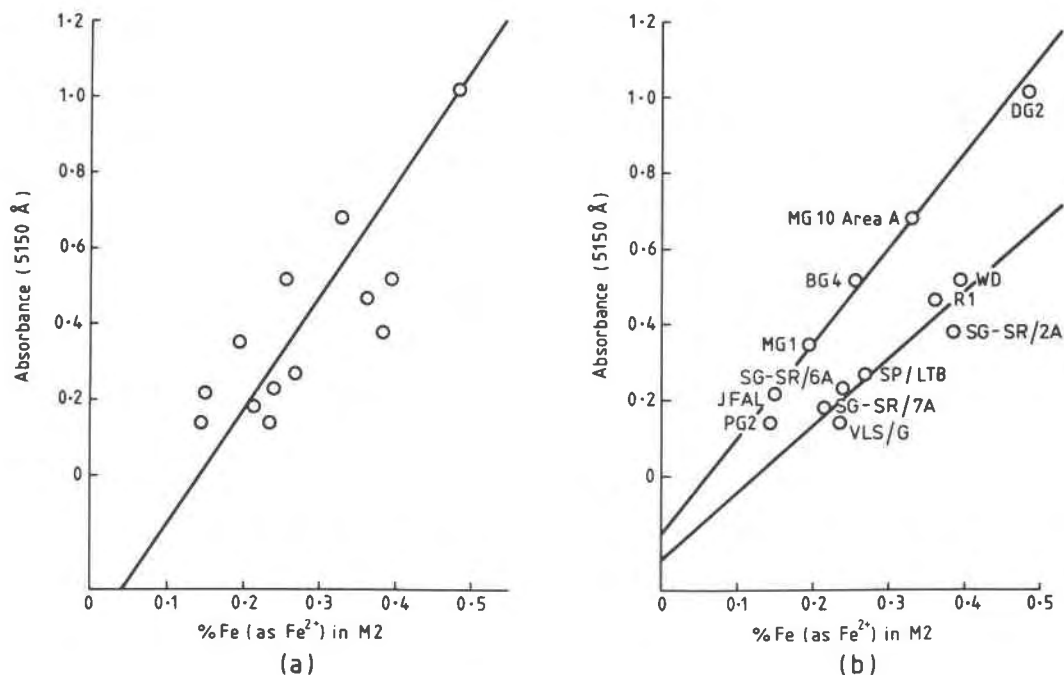


Fig. 3. The relationship between background absorption at 5150Å and Fe^{2+} in the M2 site in the studied muscovites.

and red-green muscovites in another. (Substantially the same plots were obtained at other wavelengths between 4000 and 5000Å). Finch (1963) showed that log absorbance at 4950Å and optical crystallographic properties were linearly related within muscovites of particular color groupings. It is of interest therefore that within somewhat similar color groupings of the present study, the background absorption is related to the Fe^{2+} concentration of the M2 site. In view of this relationship it is reasonable to propose that the absorption arises predominantly from metal-ligand ($\text{Fe}^{2+} \rightarrow \text{O}$) charge transfer as suggested by Robbins and Strens (1972) for some biotites, but with the additional point that for these muscovites it is the $\text{Fe}^{2+}(\text{M2}) \rightarrow \text{O}$ charge transfer. The possibility of absorption due to Fe^{3+} clusters (Kliem and Lehmann, 1979) cannot be dismissed entirely but, in the present muscovites, it is unlikely to be a dominant mechanism for absorption in the UV-blue region in view of the lack of correlation with the Fe^{3+} content. Further, there is no evidence of clustering of Fe^{3+} in muscovites from ESR measurements. Published spectra by Kemp (1973) established clearly that the Fe^{3+} resonances arise from single, magnetically dilute Fe^{3+} ions. Similar results were obtained at this laboratory for some green muscovites (*i.e.*, probably high in Fe^{3+}) which were similar to those used in the present

study. Again, in the PG2 specimen (comparatively high in Fe^{3+}), the absorption is low in the 4800–5800Å region where, by comparison with biotites, one might expect to observe two Fe^{3+} cluster absorption peaks (Kliem and Lehmann, 1979). This was even more clearly demonstrated in a very pale green muscovite (PG1) reported by Finch (1963), in which a sharply defined peak at 4430Å (shown below to arise from an Fe^{3+} ligand field transition) was accompanied by such a sharp drop in absorption with increasing wavelength that it could not be measured above 5000Å.

The sharp absorption maximum (B, Fig. 2) at 4430Å (22600 cm^{-1}) is clearly correlated with Fe^{3+} content of the muscovites and has been assigned by Faye (1968a) as the spin forbidden d-d transition ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1, {}^4\text{E}$. There seems no reason to doubt this assignment. Faye also assigned peaks at 19650 cm^{-1} (5080Å), 17200 cm^{-1} (5810Å) and 14700 cm^{-1} (6800Å) to spin forbidden d-d transitions of Fe^{3+} . Features were certainly observed at the two former wavelengths (see for example WD, Fig. 2) in many of the muscovites but, as discussed below, we cannot agree that they arise from d-d transitions.

It is convenient to treat the absorbance maximum (C) at 5080Å and the broad band (D) together (Fig. 2); indeed it may be that they are both part of the same metal-metal charge transfer system. Howev-

er, in many of the samples studied (see also Finch, 1963) there seemed to be evidence of a reasonably well defined absorbance maximum at 5080Å. Peaks in this region have been assigned to spin-forbidden ${}^6A_1 \rightarrow {}^4T_2$ d-d transition of Fe^{3+} (Faye, 1968a), and to a composite band consisting of metal-metal charge transfer bands (both mixed and similar metals) and to $Ti \rightarrow O$ metal-ligand charge transfer (Robbins and Strens, 1972 and Smith, 1977). The present work, however, establishes that the 5080Å peak and the broad band at 5000–6000Å are clearly related to the Fe^{2+} concentrations in the muscovites but in no simple way. The features are, for example, most pronounced for the red muscovites (see WD, Fig. 2) and almost absent for the 'pure green' (PG2, Fig. 2). The peak at 5080Å cannot therefore generally be a spin-forbidden d-d transition of Fe^{3+} as suggested by Faye; the very small absorption maximum at 5080Å in PG2 (Fig. 2), which is highest in Fe^{3+} , may however be such a transition. Further, there are no possible d-d transitions of Fe^{2+} in this spectral region; the spin-allowed ${}^5T_2 \rightarrow {}^5E$ d-d transition of octahedrally coordinated Fe^{2+} is expected to be in the near infrared close to 10,000Å. (In a few of the high ferrous muscovites of this study, absorption bands were observed near 9000Å and 11,000Å corresponding (Faye, 1968a) to the Jahn Teller components of the ${}^5T_2 \rightarrow {}^5E$ transition of Fe^{2+}).

It follows that the 5000–6000Å features of the present spectra arise from $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer together with, possibly, contributions from $Fe^{2+} \rightarrow Ti^{4+}$ charge transfer and/or $Ti \rightarrow O$ metal-ligand charge transfer. Such titanium charge transfer contributions are suggested by DG-2 which (Fig. 2) has the greatest absorbance and the highest titanium content (Table 1). However, there is no consistent relationship between the absorbance intensity scale of Figure 3(b) or any other absorption feature and the titanium content. We therefore propose that the spectral features from 5000 to 6000Å are dominantly determined by $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer bands which will tend to mask absorption from other charge transfer bands. The intensity of the former bands depends upon Fe^{2+} , Fe^{3+} ions in adjacent edge-sharing octahedra. In the dioctahedral micas, there are two possibilities: first, charge transfer between ions in edge-sharing M1, M2 sites and, second, charge transfer between two edge-sharing M1 sites. The first of these is twice as probable as the second in the absence of any preferential ordering, or pairing of Fe^{2+} and Fe^{3+} in

the M1 and M2 sites. Such preferential ordering or pairing could be expected to profoundly affect the intensities of $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer bands (see for example Smith, 1978). Present results seem to indicate that there are contributions from both Fe^{2+} (M2) $\rightarrow Fe^{3+}$ (M1) and Fe^{2+} (M1) $\rightarrow Fe^{3+}$ (M1) with the former being predominant. For example, Figure 4 shows the plot of the integrated intensity of the 5000–6000Å band versus the ratio of relative number of ions Fe^{2+} (M2)/ Fe^{3+} (M1). Except for three of the muscovites studied the linear correlation is convincing.

The small broad absorption maximum at 4700Å occurs in all the muscovites studied but it cannot be related to any of the various properties discussed above. Faye (1968a) assigned a peak at this wavelength to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of Ti^{3+} but the analytical results of Table 1 do not show any correlation between Ti content and peak intensity. This assignment must therefore be regarded as rather uncertain. Alternatively it could be suggested that the peak may correspond to the middle one of three bands (at 4140Å, 4880Å, 5840Å) assigned by Kliem and Lehmann (1979) to Fe^{3+} clusters in biotites. However, there is no correlation between the intensity of the observed peak and Fe^{3+} concentration in the muscovites of this study.

It had been hoped, as part of this study, to relate the pleochroism observed from the polarized spectra in the basal plane to the various properties discussed above. Although some correlations ap-

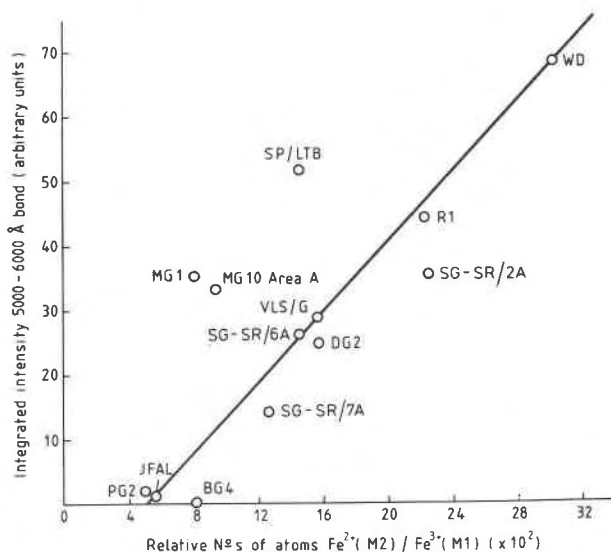


Fig. 4 Integrated intensity of the 5000–6000Å band vs. ratio of relative number of ions Fe^{2+} (M2)/ Fe^{3+} (M1) in the studied muscovites.

peared possible, they were usually applicable only to a limited color grouping, as for example within the medium-dark green group or within the pure green specimens. No significant conclusions could, therefore, be drawn for the overall series of muscovites. One interesting, but unexplained, feature of the *Y,Z* absorption spectra was observed for the bands at 5000–5800 Å and the peak at 5080 Å (previously noted within members of the SG-SR series for this peak only (Finch, 1963)). In the green-red muscovites SG-SR/2A, SG-SR/6A, SG-SR/7A and VLS/G, the intensities of these bands is measurably greater in the *Z* vibration direction; for all the other specimens, the reverse is true. In contrast, the peak (B) at 4430 Å, which has been assigned to an Fe³⁺ ligand field transition, and which correlates well with Fe³⁺ concentration, is always more intense in the *Z* than in the *Y* vibration direction in all the specimens studied. It seems likely, therefore, that the observations above for the 5000–5800 Å region, which do not appear to correlate with any of the structural, compositional or color factors discussed above, could be an indication of Fe²⁺ and/or Fe³⁺ ordering in the M1 and M2 sites.

Conclusion

In agreement with earlier suggestions for muscovites it has been shown that color arises dominantly from Fe²⁺ and Fe³⁺ in common pegmatitic muscovites. By judicious choice of samples, complicating contributions from other transition metals such as Mn, V and Cr and probably also from titanium have been eliminated. Crucial to the understanding of color and absorption of the muscovites studied is the distribution of Fe²⁺ and Fe³⁺ in the octahedral layer. In particular the concentration of Fe²⁺ in the normally unoccupied M2 site appears to have a dominant affect on the absorption properties. Background absorption is determined largely by the intense Fe²⁺ (M2) → O metal-ligand charge transfer band which peaks in the UV and “tails” in the visible. The presence or absence of various Fe²⁺–Fe³⁺ metal–metal charge transfer bands then provide, alternatively, transmission “blinds” or “windows” giving rise to the various green and red hues common in pegmatitic muscovites.

In further work it is planned to study absorption and Mössbauer Fe²⁺, Fe³⁺ assignments for a larger number of common pegmatitic muscovites within a single well defined color grouping with the expectation of obtaining more quantitative relations. Also,

single crystal Mössbauer measurements are to be carried out on specimens similar to the “end member” muscovites PG2 and WD with a view to relating electric field gradient (EFG) and optical absorption features.

Acknowledgments

We are indebted to Dr. L. P. Aldridge for the Mössbauer fitting program and for valuable discussions, to Mr. J. Patterson for the atomic absorption analyses and to Mr. J. Hunt of Soil Bureau, DSIR, for the XRF analyses.

References

- Aldridge, L. P., Bancroft, G. M., Fleet, M. E., and Herzberg, C. T. (1978) Omphacite studies. II. Mössbauer spectra of C2/c and P2/n omphacites. *American Mineralogist*, 63, 1107–1115.
- Askvik, H. (1972) Red muscovite from a metasedimentary gneiss, Sogn, West Norway. *Shrifter, Norges geologiske undersøkelse*, 273, 7–11.
- Bancroft, G. M. (1973) *Mössbauer Spectroscopy; An Introduction for Inorganic Chemists and Geochemists*. Wiley, New York.
- Bancroft, G. M. and Brown, J. R. (1975) A Mössbauer study of coexisting hornblendes and biotites: quantitative Fe³⁺/Fe²⁺ ratios. *American Mineralogist*, 60, 265–272.
- Bowen, L. H., Weed, S. B., and Stevens, J. G. (1969) Mössbauer study of micas and their potassium-depleted products. *American Mineralogist*, 54, 72–84.
- Dowty, E. and Lindsley, D. H. (1973) Mössbauer spectra of synthetic hedenbergite-ferrosilite pyroxenes. *American Mineralogist*, 58, 850–868.
- Faye, G. H. (1968a) The optical absorption spectra of certain transition metal ions in muscovite, lepidolite, and fuchsite. *Canadian Journal of Earth Sciences*, 5, 31–38.
- Faye, G. H. (1968b) The optical absorption spectra of iron in six-coordinate sites in chlorite, biotite, phlogopite and vivianite. Some aspects of pleochroism in the sheet silicates. *Canadian Mineralogist*, 9, 403–425.
- Finch, J. (1963) A colorimetric classification of Australian pegmatitic muscovite. *American Mineralogist*, 48, 525–554.
- Goodman, B. A. (1976) The Mössbauer spectrum of a ferrian muscovite and its implications in the assignment of sites in dioctahedral micas. *Mineralogical Magazine*, 40, 515–517.
- Hogg, C. S. and Meads, R. E. (1970) The Mössbauer spectra of several micas and related minerals. *Mineralogical Magazine*, 37, 606–614.
- Kemp, R. C. (1973) Electron spin resonance of Fe³⁺ in muscovite. *Physica Status Solidi (Section) B: Basic Research*, 57, k79–81.
- Kliem, W. and Lehmann, G. (1979) A reassignment of the optical absorption bands in biotites. *Physics and Chemistry of Minerals*, 4, 65–75.
- Marfunin, A. S., Mineyeva, R. M., Mkrtchyan, A. R., Nyussik, Ya. M. and Fedorov, V. Ye. (1969) Optical and Mössbauer spectroscopy of iron in rock-forming silicates. *International Geology Review*, 11, 31–44.
- Richardson, S. M. (1975) A pink muscovite with reverse pleochroism from Archer's Post, Kenya. *American Mineralogist*, 60, 73–78.
- Richardson, S. M. (1976) Ion distribution in pink muscovite: a reply. *American Mineralogist*, 61, 1051–1052.

- Robins, D. W. and Strens, R. G. J. (1972) Charge-transfer in ferromagnesian silicates: The polarized electronic spectra of trioctahedral micas. *Mineralogical Magazine*, 38, 551-563.
- Ruthberg, S., Barnes, M. W., and Noyce, R. H. (1963) Correlation of muscovite sheet mica on the basis of color, apparent optic angle, and absorption spectrum. *Journal of Research of the National Bureau of Standards—A. Physics and Chemistry*, 67A, 309-324.
- Smith, G. (1977) Low-temperature optical studies of metal-metal charge-transfer transitions in various minerals. *Canadian Mineralogist*, 15, 500-507.
- Smith, G. (1978) Evidence for absorption by exchange-coupled Fe^{2+} - Fe^{3+} pairs in the near infra-red spectra of minerals. *Physics and Chemistry of Minerals*, 3, 375-383.
- Smith, G. and Strens, R. G. J. (1976) Intervalence Transfer Absorption in Some Silicate, Oxide and Phosphate Minerals. In R. G. J. Strens, Ed., *The Physics and Chemistry of Minerals and Rocks*, p. 583-612. Wiley, New York.

*Manuscript received, January 9, 1981;
accepted for publication, September 16, 1981.*