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Ion distribution in pink muscovite, a discussion

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Introduction

Recently, Richardson (1975) presented an investigation of pink muscovite from Archer's Post in Kenya, in which he used Mössbauer spectroscopy and optical-absorption technique. He argued that ferric iron, tetrahedrally coordinated, was the major ion which gives rise to the color and the reversed pleochroism observed in that mica.

In view of the recent developments in the application of spectroscopic methods to mineral chemistry, we feel it important to draw attention to the discussion and arguments presented by Richardson in favor of the above-mentioned iron distribution in the red type of muscovite. All the evidence reported by him and additional data on similar muscovites obtained by us indicate that ferric iron in this mica type is octahedrally coordinated.

Investigated samples

Our samples of red pleochroic muscovites came from Sogn in Norway (Askvik, 1972) and Ultevis in Sweden (Ödman, 1950). Their chemical compositions and optical data are given in Table 1 and compared with the data given by Richardson (1975) for his muscovite. The analysis of Mn is given as Mn_2O_3 for the Sogn and Ultevis samples, since EPR measurements on these two samples showed no resonance pattern which could be ascribed to Mn^{2+}. This is in agreement with the suggestions made in earlier investigations of red muscovites. Comparison of the chemical and structural data indicates that they are all very similar to the muscovite investigated by Richardson.

Experimental

Mössbauer spectroscopy was performed at room temperature on randomly oriented powder or on oriented mica flakes (1–2 mg Fe/cm^2), using an electromechanical Doppler-velocity generator, operating at constant acceleration, in conjugation with a ND 512 channel analyzer. The mirror symmetrical spectra obtained (256 channels each) were folded and fitted by computer technique, using a program described by Agresti *et al.* (1969), which assumed that the absorption lines are of Lorentzian shape. The source used was ^{57}Co in Rh, and the reported Mössbauer parameters are given relative to metallic iron.

The optical spectra of the micas were recorded in unpolarized light at room temperature, using a Zeiss PMQ II, single-beam spectrophotometer equipped with a photomultiplier and a PbS cell as detectors. Spectra were measured at frequencies between 28,000 and 5,000 cm^{-1}. The spectra of micas were measured on flakes with the incident beam perpendicular to the basal plane or on powder samples, using the KBr-pellet technique. Band maxima were estimated visually from the measured spectra.

Results and discussion

Mössbauer spectroscopy

The results of the Mössbauer measurements are summarized in Table 2 and compared with the data given by Richardson (1975). No absorption lines due to ferrous iron could be detected, and all the iron can thus be assumed to be in its ferric state in agreement with the chemical analysis. Goodman (1976) reports the same Mössbauer parameters as we found for the Sogn muscovite (Table 3) and assigned ferric iron to the $M2$ octahedron (*cis*-symmetry).

Absorption measurements performed on oriented flakes at different angles yielded spectra with the well-known asymmetry commonly observed in micas (Fig. 1). This is due to the ordering of the principal axis, thus changing the relative transition probabilities of the quadrupole doublet, which is dependent on the angle between the axis of symmetry and the incident gamma ray. It should, however, be noted that the asymmetry is opposite to that found for ferrous iron octahedrally coordinated in micas (Annersten, 1975a). This will be readily understood from the opposite sign of the electric-field gradients for the two types of iron, as shown by Ingalls (1964). This asymmetry was not observed for ferric iron in ferriphlogopite (Annersten *et al.*, 1971), apparently due to the

TABLE 1. Chemical and crystallographical properties of red pleochroic muscovite

Weight Percent	Archer's Post[a]	Sogn[b]	Ultevis[c]
SiO_2	45.10	46.21	43.67
Al_2O_3	34.60	29.05	29.76
TiO_2	0.56	0.92	0.72
Fe_2O_3	2.81	4.93	4.36
FeO	0.1	0.02	nil
Mn_2O_3	0.55	0.60	0.65
MgO	0.64	2.01	1.19
CaO	0.1	0.17	0.06
BaO	0.09	nd	0.05
ZnO	0.01	nd	nd
Na_2O	0.21	0.43	0.54
K_2O	10.4	10.63	10.00
H_2O^+	4.85	4.32	5.96
F	nil	nd	0.95
Total	99.94	99.63	100.01
Optical parameters			
α	1.564		
β	1.600	1.602	1.595-1.607
γ	1.605	1.607	
2 V	41°56'	35°	38-39°
Type	$2M_1$	2M	2M

a) Richardson (1975), b) Askvik (1972), c) Ödman (1950)

greater symmetry of the tetrahedrally coordinated, ferric-iron site.

The most useful Mössbauer parameter which distinguishes ferric iron in different coordination symmetries is the isomer-shift value. The isomer-shift measures the electron density around the iron nucleus, where the contribution comes mainly from the atom's own valency electrons and from electrons from the surrounding ligands constituting the chemical bond. This interaction will thus be influenced by the bonding distances in the structure. Indeed, there is a very good correlation between the bonding distances in mineral structures and the observed isomer shifts for ferric iron (Table 3). This table shows all the measured Mössbauer parameters for undoubtedly four and six coordinated ferric irons in silicate structures, and it also shows a distinct difference in isomer shift between tetrahedrally and octahedrally coordinated ferric iron. Our and Richardson's observed values can therefore only be assigned to six coordinated ferric iron. There is also no reason to believe that the bonding situation in tetrahedral sites in pink muscovites is so different from phlogopite, as to justify the large shift reported by Richardson (1975), as being due to ferric iron in a tetrahedral site (*cf.* also Table 3). The major argument used by Richardson for tetrahedrally coordinated ferric iron was the comparison with the large isomer shift of tetrahedrally coordinated ferric iron in sanidine reported by Brown and Pritchard (1969). New measurements on several iron-containing feldspars of both natural and synthetic origin by one of us have, however, shown that the earlier-reported value was too high (Table 3).

Mössbauer data alone can thus predict whether the ferric iron in red muscovite in octahedrally coordinated or not.

Optical spectroscopy

The observed spectra of red muscovites are shown in Figure 2, and the band positions obtained are given in Table 4. All the spectra are very similar and exhibit a broad absorption shoulder between 25,000 and 15,000 cm^{-1} and a broad absorption band centered at 13,200 cm^{-1}. The broad shoulder is composed of several bands, which could be distinguished in spectra 1 and 3. Spectrum 2 (Sogn) is a powder spectrum and thus yields poorer resolution. An absorption band can also be resolved around 27,000 cm^{-1}, when measurements are made down to these low wavelengths.

As will be seen from Table 4, our site assignment of the same bands differs from that given by Richardson (1975). He assigned the bands 22,624, 21,834, 21,367, and 19,608 cm^{-1} to ferric iron, tetrahedrally coordinated. This assignment was made after comparison with the optical spectra of the Old Chelsea phlogopite (Table 5), which undoubtedly contains tetrahedrally coordinated ferric iron (Hogarth *et al.*, 1971). However, strong arguments against the assignment proposed by Richardson are also evident from this com-

TABLE 2. Hyperfine parameters of Fe^{3+} in red muscovite at room temperature

	I S mm/s	ΔE_Q mm/s	FWHH mm/s
Archer's Post, Kenya	0.46	0.73	0.82
Sogn, Norway	0.36	0.73	0.64
Ultevis, Sweden	0.41	0.66	0.68

I S relative to metallic iron. Data on Archer's Post from Richardson (1975)

Table 3. ^{57}Fe hyperfine parameters of Fe^{3+} in some minerals at 300 K, I S relative to metallic iron. Crystallographic data (Me–O) are given for Si–O or Al–O distances, unless otherwise specified

	Site	Co-ordination	Mean Me-O Å	Δ Me-O Å	I S mm/s	ΔE_Q mm/s	Reference
Schorlomite garnet	Z	4			0.19	1.13	Virgo and Huckenholtz (1974)
Diopside	Si	4	1.634	0.102	0.18	1.49	Hafner and Huckenholtz (1971)
Phlogopite	Al	4	1.649	0.003	0.19	0.44	Hogarth, Brown and Pritchard (1970)
Ferriphlogopite	Si	4	1.681(Fe)	0.021	0.17	0.50	Annersten *et al* (1971)
Sanidine	Si	4	1.662	0.025	0.21	0.48	Annersten (1976)
Fe-Al-Sanidine	Si	4			0.22	0.61	Annersten (1976)
γ-Fe_2O_3	A	4	1.89 (Fe)		0.22	0.079	Annersten and Hafner (1973)
γ-Fe_2O_3	B	6	2.06 (Fe)		0.37	0.023	Annersten and Hafner (1973)
Andradite garnet	Y	6	2.024(Fe)		0.50	0.55	Amthauer, Annersten and Hafner (1976)
Augite	M1	6	2.031(Fe)	0.218	0.45	0.84	Bancroft (1973)
Diopside	M1	6	2.031(Fe)	0.218	0.42	1.01	Hafner and Huckenholtz (1971)
Actinolite	M2	6	2.098(Fe)	0.129	0.40	0.57	Burns and Greaves (1971)
Muscovite	M2	6	1.95	0.118	0.41	0.81	Hogg and Meads (1970)
Red muscovite	M2	6	1.95	0.118	0.36	0.72	Goodman (1976)
Glauconite	M2	6			0.36	0.44	Annersten (1975b)
Biotite	M2	6	2.101(Fe)	0.029	0.42	0.50	Annersten (1974)

parison. The band intensities of the ferric-iron peaks observed at 22,624 cm^{-1} and below that value in the spectrum of the Archer's Post muscovite are almost similar when background corrections are considered. Extinction coefficients of tetrahedral ferric-iron bands, however, are shown to differ by over 100 percent (*cf.* Table 5), due to overruling the Laporte selection rule on tetrahedral symmetry (Faye and Hogarth, 1969; and Faye, 1969). None of the spectra of red-type muscovite presented in Figure 2 show such a feature, which strongly supports the hypothesis of nontetrahedral coordination of ferric iron in the present micas.

Our assignments of the ferric-iron bands (Table 4) are moreover in very good agreement with the ferric-iron bands assigned to octahedral sites in muscovite and lepidolite (Faye, 1968; *cf.* also Table 5). Similar band positions are also reported for octahedrally coordinated ferric iron in garnets (Manning, 1972; Amthauer, 1974).

The similar shape of all the spectra of this type confirms the result of the above-mentioned EPR measurements—that Mn^{2+} is not present in any of the samples. Mn^{3+} with a d^4 electron configuration is succeptible to a large Jahn-Teller distortion in octahedral coordination and is expected to show three spin allowed transitions. The bands assigned to Mn^{3+} in octahedral coordination by us are situated at

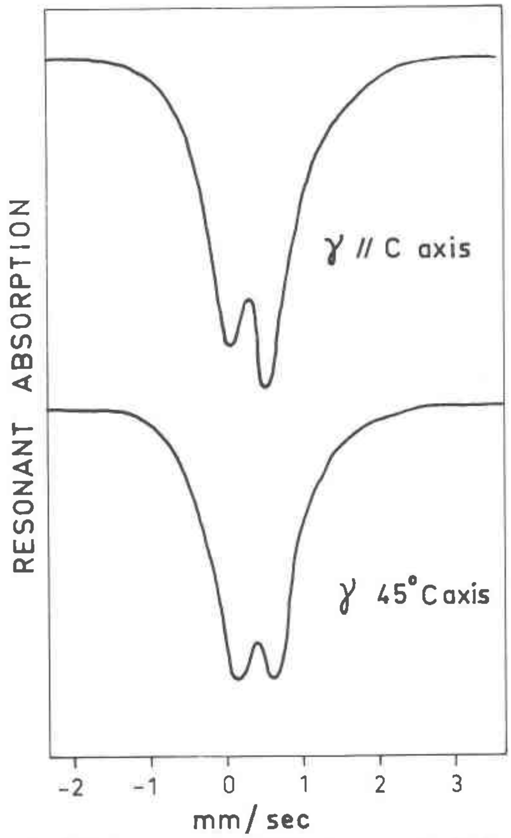

FIG. 1. Mössbauer spectra of Ultevis muscovite. Flake oriented at different angles to the incident γ-rays. Reproduced from oscilloscope picture.

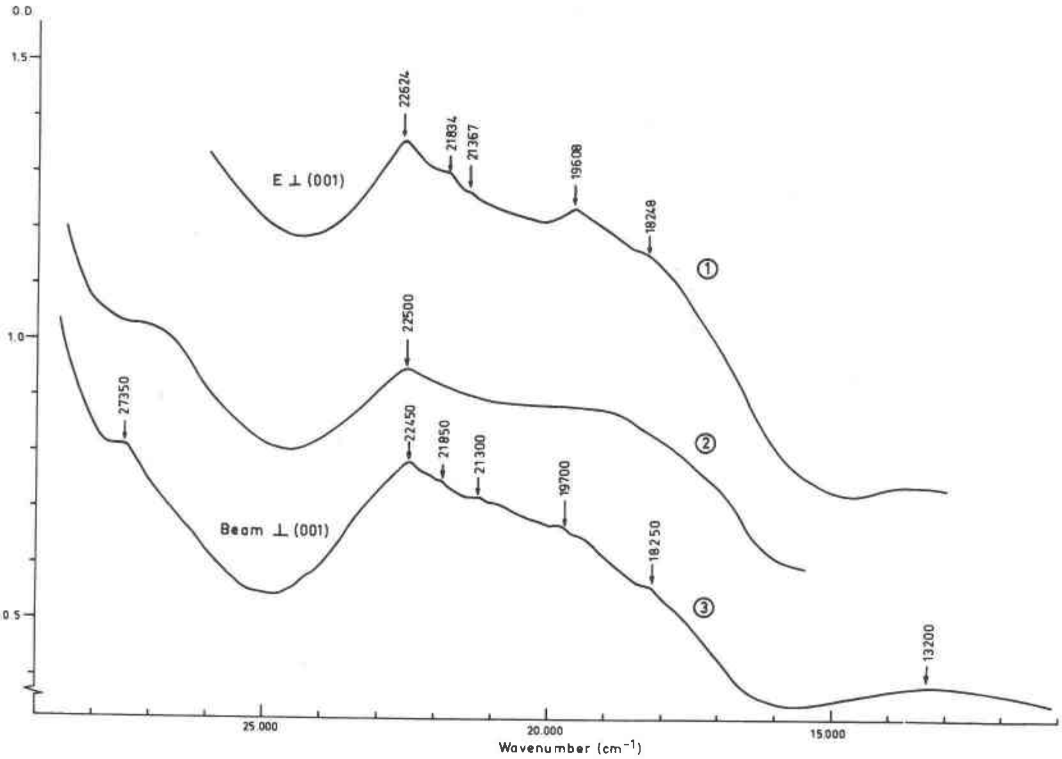

FIG. 2. Optical absorption spectra of red-type muscovite. (1) Archer's Post, Kenya (Richardson 1975), (2) Sogn, Norway (powder sample) and (3) Ultevis, Sweden (unpolarized spectrum).

21,850, 18,250, and 13,200 cm^{-1}, in good agreement with the bands due to Mn^{3+} in epidote (Burns and Strens, 1967), manganophyllite (Burns, 1970), tournamline (Manning, 1973), and viridine (Hålenius, unpublished). The relative stabilization energy of Mn^{3+} in muscovite deduced from our spectra is about 43 kcal, compared with the 46.5 kcal found for Mn^{3+} octahedrally coordinated in phlogopite (Burns, 1970).

TABLE 4. Band position and band assignments in red muscovite

Sample	Wave number cm^{-1}	Ion	Site assignment	Reference
Archer's Post, Kenya	18 248 13 700	Mn^{3+}	Octahedral	Richardson (1975)
	22 624 21 834 21 367 19 608	Fe^{3+}	Tetrahedral	
Sogn, Norway	22 250	Fe^{3+}	?	Askvik (1972)
Ultevis, Sweden	21 850 18 250 13 200	Mn^{3+}	Octahedral	This investigation
	27 350 22 450 21 300 19 700	Fe^{3+}	Octahedral	

It is also important to realize that transition elements incorporated in very distorted sites should show a pronounced variation in their absorption-band intensities with a change of the direction of polarization of the absorbed light. Such features are commonly observed for Mn^{3} (Burns, 1970) and may be the major reason for the change in intensities of the two spectra shown by Richardson. Unfortunately, the spectra of red muscovite are obviously too poorly resolved for accurate estimation of the extinction coefficients of the respective bands. However, the optical spectra of the present red muscovites also favor the assignment of both Fe^{3+} and Mn^{3+} to octahedral coordination in muscovite.

Conclusions

In view of the arguments presented above, it must be concluded that both Fe^{3+} and Mn^{3+} are octahedrally coordinated in red and pink types of muscovites. The pleochroism and color of this type of mica are thus not due to tetrahedrally coordinated iron. It may be noted that micas that undoubtedly have tetrahedrally coordinated ferric iron usually exhibit a

Table 5. Observed absorption bands in phyllosilicates

Mineral	Ion	Co-ordination	Wave number cm^{-1}	Extinction mol/l	Reference
Muscovite	Fe^{3+}	6	27 400		Faye (1968)
			26 600		
			22 600	~2	
			21 500		
			19 650		
			17 200		
			14 700		
			11 600		
Lepidolite	Fe^{3+}	6	22 800		Faye (1968)
			21 200		
			19 800		
			15 200		
			11 600		
Phlogopite	Fe^{3+}	4	22 700	~150	Faye and Hogarth (1969)
			20 300	~ 50	
			19 200		
Manganophyllite	Mn^{3+}	6	21 400		Burns (1970)
			19 050		
			14 850		

brown color (Steinfink, 1962, Faye and Hogarth, 1969), while manganous minerals often show colors shading towards pink. Askvik (1972) also suggested Ti^{3+} as a possible chromophore in red micas. Richardson rejected Ti as a chromophore since red muscovite from Pilar, New Mexico, contained no Ti. Reference to the original paper of Schaller and Henderson (1926) shows, however, that they did not analyze for Ti. Hence, the Ti content of this muscovite is not known. However, the high degree of oxidation which all these red muscovites represent (only Fe^{3+} and Mn^{3+}) makes it less likely that Ti^{3+} is stable. Burns (1972), however, reported the presence of Ti^{3+}, together with the simultaneous presence of Fe^{3+} in schorlomite garnet. There is no spectroscopic evidence of Ti^{3+} in the present micas

The color of the investigated muscovites thus seems most likely to be due to the presence of Mn^{3+} in octahedral coordination.

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