

A Reassignment of the Optical Absorption Bands in Biotites

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Abstract. The electronic absorption spectra of three biotites with largely differing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios were studied before and after thermal dehydration and oxidation of divalent iron. Three absorption bands near 17,100, 20,500 and 24,100 cm^{-1} and an absorption edge at slightly higher energies are assigned to trivalent iron present in clusters of strongly interacting ions. The presence of additional broad absorption bands due to intervalence transfer between Fe^{2+} and Fe^{3+} or Ti^{4+} in this region cannot be excluded for biotites with high Fe^{2+} concentrations. Three bands at lower energies show a satisfactory correlation with concentration of divalent iron and decrease in the same proportions with oxidation. We therefore assign them to split components of the spin-allowed ligand field transition of Fe^{2+} at the M_1 and M_2 sites. This contradicts the assignment of one of these bands to an intervalence charge transfer between Fe^{2+} and Fe^{3+} by previous authors. It is shown that there is no indisputable evidence against our assignment.

Introduction

Optical absorption spectra of biotites have been reported by several authors (Faye, 1968; Robbins and Strens, 1972; Smith and Strens, 1976; Smith, 1977). There now appears to be general agreement that the two bands of lowest energy near 8,700 and 10,900 cm^{-1} arise from spin-allowed ligand field transitions of Fe^{2+} and that a third band near 13,900 cm^{-1} is due to an intervalence charge transfer between neighboring ions of di- and trivalent iron. The assignment of this band may, however, be questioned for two reasons:

(a) The ligand field transition ${}^5T_2 \rightarrow {}^5E$ of Fe^{2+} in cubic symmetry normally splits into two resolved components as a result of the Jahn-Teller effect and low site symmetries. There are two nonequivalent hexacoordinated sites, M_1 and M_2 , for divalent ions in the structure of trioctahedral micas (Donnay et al., 1964; Franzini and Schiaffino, 1964), and Mössbauer investigations have

shown the presence of divalent iron at both sites in biotites (Hogg and Meads, 1970, 1975; Annersten, 1974; Häggström et al., 1969). Thus up to four ligand field bands can be expected in the near infrared region for Fe^{2+} in biotite.

(b) Absorption bands arising from intervalence transfer are usually significantly broader than ligand field bands. Although the absorption bands of biotites overlap considerably even at low temperatures, their decomposition into components of Gaussian shape yields bands of comparable halfwidths in the range between 2,500 and 3,500 cm^{-1} expected for ligand field transitions.

The origin of additional absorption bands at higher energies is still unknown. The proposed assignment to spin-forbidden transitions of divalent iron (Faye, 1968) is definitely wrong, since their intensities are several orders of magnitude too high.

Oxidation of divalent iron in biotites by heat treatment has been studied before using various different methods including thermogravimetry and differential thermal analysis (Rimsaite, 1967, 1970; Vedder and Wilkins, 1969), Mössbauer spectroscopy (Hogg and Meads, 1975; Kotlicki et al., 1976) and infrared absorption (Vedder and Wilkins, 1969). Apparently optical absorption has not yet been employed although it offers a unique possibility to check the assignments of these bands, since the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be changed within wide limits while the total concentration of iron and other metal impurities remains unchanged. For this purpose oxidation of two biotites with differing initial $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios was investigated via infrared and optical absorption. In addition, the electronic absorption spectrum of a natural biotite without appreciable content of divalent iron was also studied.

Experimental

Three different biotites were used in the present study:

- (1) a reddish natural biotite from Kronenburg, Eifel,
- (2) a brownish black biotite with low fluorine content and
- (3) a brownish black biotite with higher fluorine content.

From these biotites cleaved plates with thicknesses down to 10 μm were used allowing measurement of absorption coefficients as high as 2,000 cm^{-1} . Their thicknesses were determined from the spacings of the regular interference patterns which are easily resolvable in the near infrared, according to the equation

$$d = \frac{z \cdot \lambda_1 \cdot \lambda_2}{2n(\lambda_2 - \lambda_1)}$$

with z = number of maxima in the wavelength range between λ_1 and λ_2 and n = refractive index.

Optical absorption spectra normal to the (001) cleavage plane were recorded on a Beckman DK 2A spectrophotometer at 300 and 78 K with the sample mounted in a suitable cryostat. In some cases polarized absorption spectra were measured employing polarizing foils (type HR from Polaroid Corporation for the near infrared and type PB from Polacoat Corporation for the visible

and near UV ranges). Infrared spectra in the OH stretching vibration region (between 3,400 and 3,700 cm^{-1}) were recorded on a Grubb Parsons Spectromajor infrared spectrometer. The original spectra were resolved into their components with the restriction that the maximum and halfwidth of each band must be the same in all spectra if measured under identical conditions. The absorption edge at high energies was subtracted, by extrapolation of the observed linear increase with wavenumber of the absorbance logarithm, into the overlap region with the less intense absorption bands at lower energies.

The samples were heated in air for periods of 12 h at temperature intervals of 100 K, ranging between 673 and 973 K in a temperature controlled electrical furnace.

The total iron content of the biotites was determined spectrophotometrically as the $[\text{Fe}(\text{dipy})_3]^{2+}$ complex, whereas the content of divalent iron was determined separately employing the vanadate method (Wilson, 1960). In both cases calibration curves were determined, and the errors are estimated to be smaller than 10%.

Results

1. Properties of the Original Biotites

The concentrations of di- and trivalent iron in the original biotites are listed in Table 1. The optical absorption spectrum of the red biotite with almost all iron in the trivalent state is shown in Fig. 1. It can be decomposed into three Gaussian bands with maxima near 17,100, 20,500 and 24,100 cm^{-1} . The remaining absorption edge is consistent with a much more intense band (oscillator strength near 0,1) near 34,000 cm^{-1} . This extrapolation is, of course, subject to large errors. Anisotropy of these absorption bands (for the electric vector in the basal plane) is considerable with f_γ/f_β between 1.5 and 3.1. The intensities appear to increase slightly when lowering the temperature from 300 to 78 K, with an average change of -13%. The numerical data for these bands (at 300 K) are included in Table 2.

The absorption spectra of the other two biotites show bands in the same positions, but in addition three absorption bands on the low energy side are found at 8,700, 10,900 and 13,900 cm^{-1} which are in good agreement with

Table 1. Content of di- and trivalent iron of the biotites

sample no	1	2	3
FeO (wt %)	0.39	18.0	16.3
Fe ²⁺ (mol/l) ^a	0.16	7.6	6.9
Fe ₂ O ₃ (wt %)	7.4	4.6	2.0
Fe ³⁺ (mol/l) ^a	2.8	1.7	0.76
Fe ²⁺ /Fe ³⁺ ratio	0.06	4.4	9.1

^a calculated with an average density of 3.05 g/cm^3

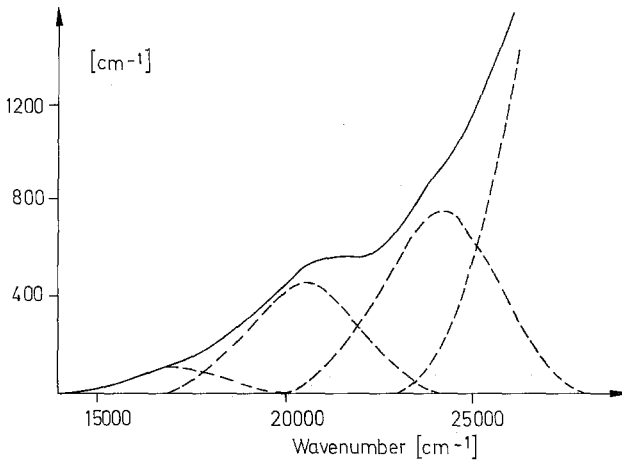


Fig. 1. Absorption spectrum of reddish brown biotite (1), measured with unpolarized light at 300 K

Table 2. Optical absorption spectra of original biotites^a

Sample no.	1		2		3		
Band position	Halfwidth	ε (cm ² /mmol)	$f \cdot 10^{3b}$	ε (cm ² /mmol)	$f \cdot 10^3$	ε (cm ² /mmol)	$f \cdot 10^3$
8,700 cm ⁻¹	2,600 cm ⁻¹	—	—	40	0.48	43	0.51
10,900	2,300	—	—	47	0.51	47	0.49
13,900	3,200	—	—	90	1.3	67	0.99
17,100	3,100	31	0.53	308	4.4	443	6.3
20,500	3,300	147	2.54	532	8.1	803	12.2
24,100	3,600	235	3.95	821	13.8	1420	23.8

^a Taken at room temperature with unpolarized light

^b Oscillator strengths are calculated from concentration of divalent iron for the first three bands and from concentration of trivalent iron for the last three bands

band positions reported by other authors (Faye, 1968; Smith and Strens, 1976; Smith, 1977). Polarization and temperature effects were studied for biotite (3) only. For all bands including those present in biotite (1) small anisotropies with f_{γ}/f_{β} near 1.1 were found. For the band at 13,900 cm⁻¹ an increase in intensity of 10% was observed between 300 and 78 K, the other bands remained unchanged in integrated intensity. The unpolarized spectrum of biotite (2) at 300 K is shown in Fig. 2 and the numerical values for these biotites are also listed in Table 2. The oscillator strengths reported in the last column of this table were calculated from the concentrations of divalent iron for the first three bands, and from the concentrations of trivalent iron for the three bands at higher energies.

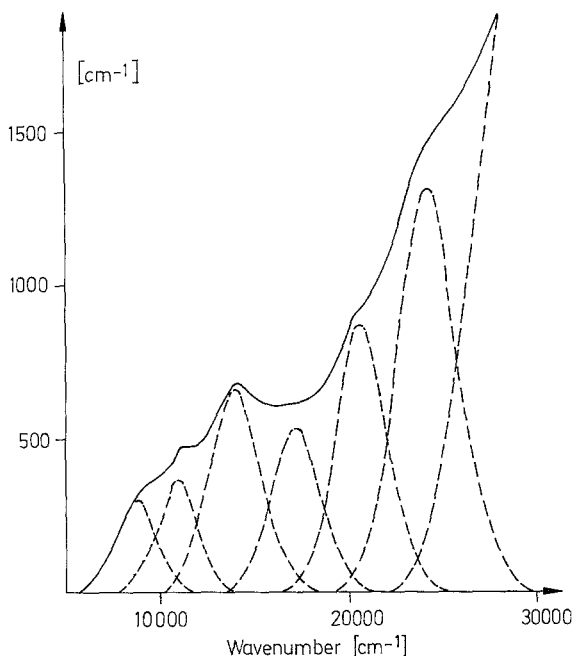


Fig. 2. Absorption spectrum of biotite (2), measured with unpolarized light at 300 K

2. Changes With Heating in Air

In the region between $3,400$ and $3,700\text{ cm}^{-1}$ two overlapping bands attributable to stretching vibrations of OH groups are found in biotite (2). The stronger one at $3,610\text{ cm}^{-1}$ has an initial extinction coefficient of 240 cm^{-1} . This band decreased to 76 and 44% of its initial value with subsequent heating at 673 and 773 K. After additional heating at 873 K it had disappeared completely. The less intense band near $3,550\text{ cm}^{-1}$ behaved in a similar way, but shifted slightly to lower energies when heated at 773 K.

The electronic absorption bands of this biotite did not change when heated at 673 K, and an apparent decrease of 6% for the band at $13,900\text{ cm}^{-1}$ is within the limits of error of our measurements. With further heating at 773 K the three bands at lower energies decreased by about 18% (18, 15, 21% were measured in order of increasing energy compared to the original values), whereas the bands at higher energies remained unchanged. With additional heating at 873 K the three bands at lower energies showed a very slight further decrease to about 80% of their original values (82; 78 and 79%) and the bands at $17,100$, $20,500$ and $24,100\text{ cm}^{-1}$ increased by 64, 100 and 93% respectively.

Somewhat different results were obtained for biotite (3) with higher content of fluorine: After heating at 873 K the three low energy bands had decreased by an average of 27% (24, 30, and 28%), whereas the bands at higher energies showed only an insignificant increase of 4%. Heating at 973 K resulted in delamination of this biotite, evident from increased reflection losses in the optical

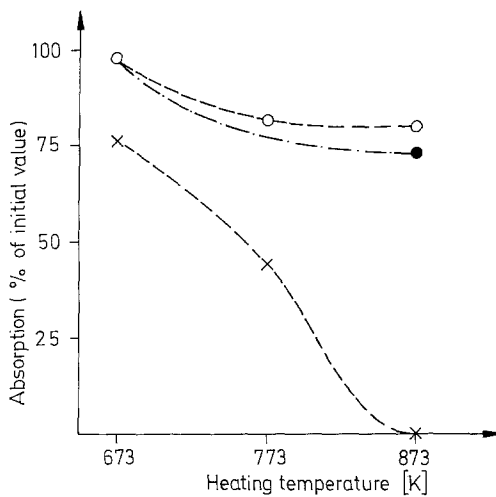


Fig. 3. Changes in the absorption spectra of biotites (2) and (3) with heating in air: x - OH band at $3,610\text{ cm}^{-1}$ in biotite (2); o and ● - average of the three low energy electronic absorption bands in biotite (2) and (3) respectively

absorption measurements, but no changes of intensities were observed for the absorption bands.

These changes for the OH and low energy electronic absorption bands are visualized in Fig. 3.

Discussion

1. Origin of the High Energy Absorption Bands

According to our results the electronic absorption bands of biotites fall into two groups. The three bands at higher energies (and the absorption edge) must be attributed to trivalent iron since they are present in the red biotite with very low concentration of divalent iron. Their oscillator strengths (between $5 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$ in this biotite) are too high to assign them to spin-forbidden ligand field transitions of isolated Fe^{3+} ions. They may, however, be due to clusters of magnetically interacting Fe^{3+} ions. Spectra of such clusters have been studied and partly assigned to certain species in aqueous solutions and in glasses. For the red dimer $[(\text{H}_2\text{O})_4\text{Fe}_{\text{OH}}^{\text{III}}\text{Fe}(\text{H}_2\text{O})_4]^{4+}$ an intense absorption band at $20,800\text{ cm}^{-1}$ was found (Wulfing et al., 1967). In addition to a band in this region, an aqueous solution of $\text{Fe}(\text{ClO}_4)_3 \cdot 10\text{H}_2\text{O}$ slowly develops stronger absorption bands at $24,000$ and $27,000\text{ cm}^{-1}$ and trivalent iron in alkali silicate glasses shows a more than linear increase of optical absorption in the region between $27,000$ and $29,000\text{ cm}^{-1}$ (Steinmann, 1971). Increased intensities of the spin-forbidden bands and additional absorption bands due to simultaneous pair excitations with formation of magnetically coupled pairs in crystals were also observed for Fe^{3+} in corundum (Krebs and Maisch, 1971) and for the isoelectronic Mn^{2+} (McClure, 1963; Ferguson et al., 1967; Lohr and McClure, 1968). In these cases early stages of clustering with a predominant presence of isolated ions and pairs are observed. In the biotites with considerably higher average concentrations of the paramagnetic ion, however, clusters of more than two ions must predominate. This is evident from electron paramag-

netic resonance (epr) measurements for the red biotite which showed a broad and isotropic signal at a g -factor of 2, but no signals from isolated Fe^{3+} ions. The halfwidth of 20 mT for the broad band is on the upper limit of halfwidths observed for precipitates of MnCl_2 in alkali halides (Oshima et al., 1955; Forrester and Schneider, 1956; Low, 1956; Watkins, 1959; Iri and Kuwabara, 1967) and of an Fe (III) compound in quartz (Stock and Lehmann, 1977). In these systems the halfwidths evidently increase with particle size of the precipitates. The absorption spectra of amarantite, a compound containing tetrameric clusters of trivalent iron, show broad bands above $17,000\text{ cm}^{-1}$ and a low energy absorption edge very similar to biotites (Rossman, 1976).

The strong absorption leading to the absorption edge near $25,000\text{ cm}^{-1}$ can be assigned to the first charge transfer band of Fe^{3+} . For Fe^{3+} surrounded by six oxygen ions in an undistorted octahedral coordination this band is expected at $41,000\text{ cm}^{-1}$ (Lehmann, 1970). Due to the lower optical electronegativity of OH of about 3, 1 (Lehmann and Gudat, 1974), this band shifts to lower energies with partial substitution of O^{2-} by OH^- and the low site symmetries of this ion in biotite lower the position of the charge transfer band still further (Lehmann, 1970). Thus the extrapolated value of $34,000\text{ cm}^{-1}$ is in reasonable agreement with expectations and lends support to our interpretation.

The intensity ratios of the three bands attributed to trivalent iron differ considerably between the red biotite and the other two, but after heating to 873 K these ratios are nearly equal in biotite (2). These ratios are, of course, subject to considerable errors due to the uncertainties inherent in the background subtraction and curve resolution processes. The calculated oscillator strengths of these bands in the red biotite are considerably lower than for the other biotites as seen from Table 2. There are, in our opinion, four obvious possibilities for this discrepancy:

(a) Only a (variable) part of the trivalent iron contributes to these absorption bands and the calculated oscillator strengths represent lower limits only. The postulated clusters of Fe^{3+} as the cause of these bands offer a plausible explanation for this incomplete correlation of intensities with total concentration of trivalent iron. The results of the heating experiments are consistent with this interpretation.

(b) In the biotites with considerable contents of both di- and trivalent iron, absorption from other sources may overlap with those due to clusters of trivalent iron. Apparently, this additional absorption should be strongest in the region of the band at $17,100\text{ cm}^{-1}$. Intervalence charge transfer between divalent iron and either trivalent iron or tetravalent titanium offers a likely mechanism for this additional absorption in samples with higher concentration of divalent iron. The titanium contents of our biotites were not determined, but data from the literature (Larsen et al., 1937; Foster, 1960; Deer et al., 1962; Dodge et al., 1969) indicate concentrations between 2 and 4 wt % TiO_2 in most biotites, comparable to the initial concentrations of Fe_2O_3 in our biotites (2) and (3). Due to the large halfwidths of intervalence charge transfer bands it is very difficult to identify and to subtract such additional absorptions from the three bands due to trivalent iron in this region, but the band positions and halfwidths for the red biotite obtained from curve resolution were smaller than for the

other two samples favoring the presence of additional broad absorption in the biotites (2) and (3). (The values quoted in Table 2 represent averages for all three biotites).

(c) Variable distributions of Fe^{3+} between $M1$ and $M2$ sites in combination with different contributions to the optical absorption spectra might also cause incomplete correlations. Annersten (1974) observed ratios of $M1$ and $M2$ site occupation between 1.0 and 5.3.

(d) The absorption spectra of clusters bridged by OH^- might be appreciably different from those for clusters bridged by O^{2-} ions. Since the absorption in this region remains essentially unchanged with at least partial dehydration (see next chapter) this explanation seems less likely.

The different polarization ratios for these bands in biotites (1) and (3) also suggest a superposition of bands from different origins in this region.

2. Characteristics of the Bands at Lower Energies

The absolute values of the oscillator strengths as well as their ratios for the three bands at lower energies in the biotites (2) and (3) are fairly constant. From the concentrations of di- and trivalent iron shown in Table 1 the intensity of the band at $13,900\text{ cm}^{-1}$ should be three times higher in biotite (2) than in biotite (3) if the assignment to an intervalence charge transfer between Fe^{2+} and Fe^{3+} (Faye, 1968; Robbins and Strens, 1972; Smith and Strens, 1976; Smith, 1977) is correct. Clearly such a ratio is outside the limits of error of our results. We therefore assign this band to a split component of the ${}^5T_2 \rightarrow {}^5E$ ligand field transition of Fe^{2+} . This interpretation apparently contradicts the results of Robbins and Strens (1972). They were able to correlate the intensity of this band in different micas with the product of the concentrations of di- and trivalent iron. As shown in Fig. 4, however, their data can also be correlated with the concentration of divalent iron alone. The sum of the squared deviations for this correlation is only 5% larger than for the correlation with the product of concentrations. Evidently the concentration ratios in their micas (molar ratios between 2.7 and 3.9 compared to a range between 0.06 and 9.1 for our samples) vary too little to allow a definite decision between these alternatives. The slightly differing intensity ratios of the three bands in our biotites can be explained with the assumption of a variable distribution of Fe^{2+} between the $M1$ and $M2$ sites. Annersten (1974) observed ratios between 0.6 and 1.3 for this distribution in six biotites. This variation is large enough to account for the observed variation of intensity ratios. The different fluorine content can also cause differences in oscillator strength: The parity forbidden ligand field bands gain most of their intensity from admixture of charge transfer states (Lehmann and Gudat, 1974; Eppels and Lehmann, 1977). Due to the lower optical electronegativity of OH^- compared to F^- these charge transfer bands occur at higher energies and the admixture is thus reduced for F^- as ligand. This effect should be most pronounced for the ligand field bands of highest energy. Assignment of the three bands to either $M1$ or $M2$ sites requires correlation with other data, e.g. Mössbauer spectra.

The increase of intensity for the band at $13,900\text{ cm}^{-1}$ with decreasing temperature has also been taken as evidence for its assignment to an intervalence

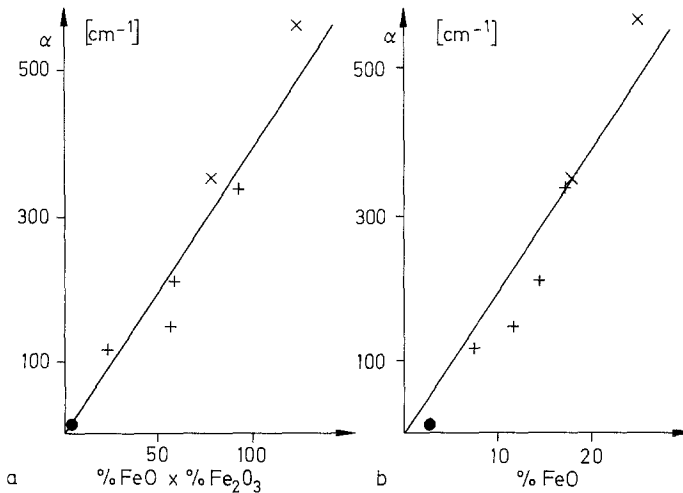


Fig. 4a and b. Correlation of extinction coefficient at $13,900\text{ cm}^{-1}$ with iron content in different micas. ● - phlogopite, x - lepidolites, + - biotites. **a** (left): Correlation with product of concentrations of di- and trivalent iron. **b** (right): Correlation with concentration of divalent iron. Data from Robbins and Strens (1972)

charge transfer (Smith and Strens, 1976; Smith, 1977). Evidently this increase is more pronounced at temperatures below 78 K. In the absence of a satisfactory explanation for this unusual temperature dependence (reversed from the increase of forbidden bands due to a vibronic mechanism) we feel that this temperature dependence alone does not yet constitute convincing evidence for an intervalence charge transfer, especially in cases where other pieces of evidence severely question this assignment.

3. Changes With Heating

At least for a nearly random oxidation of divalent iron in *M* 1 and *M* 2 sites with heating, the decrease of the ligand field bands of this ion allows a determination of the change in the ratio between di- and trivalent iron. As this ratio approaches the value of unity bands attributable to intervalence charge transfer should reach a maximum and decrease again with further decrease of this ratio. Bands attributable to trivalent iron in isolated sites should increase monotonically with oxidation. The band at $13,900\text{ cm}^{-1}$ indeed decreases monotonically and in practically the same proportion as the two bands at lower energies. This is the strongest evidence for assignment of the band at $13,900\text{ cm}^{-1}$ to a split component of the ligand field transition of Fe^{2+} . The bands attributed to clusters of trivalent iron do not increase monotonically with oxidation. This result suggests preferential oxidation of divalent iron isolated in the structure. The same conclusion was reached earlier from changes in the Mössbauer spectra of biotite with oxidation (Hogg and Meads, 1975). The strong increase of these bands when heated at 873 K in biotite (2) without significant oxidation of Fe^{2+} can be due to a redistribution of di- and trivalent iron as a result of either migration of electrons or diffusion of cations.

The final ratio of di- and trivalent iron after heating at 873 K is close to 2 in both black biotites. Clearly this is not the ultimate stage of oxidation achievable as the composition of the red biotite shows. The constant ratio for these two samples thus appears to be largely fortuitous, but resistance of a biotite against further oxidation was also observed by Kotlicki et al. (1976).

The infrared bands with maxima near $3,550$ and $3,610\text{ cm}^{-1}$ are due to OH adjacent to metal ion vacancies (Vedder, 1964; Wilkins, 1967). Preferential loss of this hydrogen due to dehydration was observed by Vedder and Wilkins (1969). Figure 3 indicates that this dehydration occurs at lower temperatures than oxidation of iron, in agreement with the results of Vedder and Wilkins. Dehydration alone evidently does not affect the optical spectra of iron in biotite significantly.

Conclusion

According to the results presented here the absorption bands of biotites can be grouped into two classes: three bands with maxima below $14,000\text{ cm}^{-1}$ due to ligand field transitions of divalent iron in M_1 and M_2 sites, and three bands above $17,000\text{ cm}^{-1}$ (as well as an absorption edge near $25,000\text{ cm}^{-1}$) due to clusters of trivalent iron. Data from the literature taken as evidence for the assignment of one of the first three bands to an intervalence charge transfer between di- and trivalent iron are also consistent with our interpretation. Thus at least no prominent bands due to an intervalence charge transfer mechanism were observed, but there may be broad and weak bands of this origin in biotites with high content of divalent iron in the region above $17,000\text{ cm}^{-1}$. Considerably more work is needed to settle this point. These future investigations should involve measurements by as many different methods as possible and may also help to fully elucidate the detailed mechanisms of oxidation and dehydration of biotites. The effects of reduction with hydrogen on the optical spectra of oxidized and dehydrated biotites should also be investigated in this connection.

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References

- Annersten, H.: Mössbauer studies of natural biotites. *Am. Mineral.* **59**, 143–151 (1974)
- Deer, W.A., Howie, R.A., Zussman, J.: *Rock Forming Silicates*, 3. Sheet Silicates. London: Longmans 1962
- Dodge, F.C.W., Smith, V.C., Mays, R.E.: Biotites from granitic rocks of the Central Sierra Nevada batholith, California. *Petrol.* **10**, 250–271 (1969)
- Donnay, G., Morimoto, N., Takeda, H., Donnay, J.D.H.: Trioctahedral one-layer micas. I. Crystal structure of synthetic iron mica. *Acta Cryst.* **17**, 1369–1373 (1964)
- Eppels, K., Lehmann, G.: Intensities of ligand field bands for hexa-co-ordinated copper (II) and nickel (II) in pure and doped single crystals. *J. Chem. Res. (S)* pp. 284–285, 1977, *J. Chem. Res. (M)* 3169–3197 1977
- Faye, G.H.: Optical absorption spectra of iron in six-coordinate sites in chlorite, biotite, phlogopite and vivianite. Some aspects of pleochroism in the sheet silicates. *Can. Mineral.* **9**, 403–425 (1968)

- Ferguson, J., Guggenheim, H.J., Tanabe, Y.: Simultaneous electronic excitation of exchange-coupled pairs of manganese and nickel ions. *Phys. Rev.* **161**, 207–212 (1967)
- Forrester, P.A., Schneider, E.E.: Paramagnetic resonance of manganese in single crystals of alkali halides. *Proc. Phys. Soc.* **69B**, 833–837 (1956)
- Foster, M.B.: Interpretation of the composition of trioctahedral micas. *US Geol. Surv. Prof. Pap.* **354B**. (1960)
- Franzini, M., Schiaffino, L.: On the crystal structure of biotites. *Z. Krist.* **119**, 297–309 (1964)
- Häggström, L., Wäppling, R., Annersten, H.: Mössbauer study of oxidized iron silicate minerals. *Phys. Status Solidi* **33**, 741–748 (1969)
- Hogg, C.S., Meads, R.E.: The Mössbauer spectra of several micas and related minerals. *Mineral. Mag.* **37**, 606–614 (1970)
- Hogg, C.S., Meads, R.E.: A Mössbauer study of thermal decomposition of biotites. *Mineral. Mag.* **40**, 79–88 (1975)
- Iri, T., Kuwabara, G.: Paramagnetic resonance of Mn^{2+} in CsBr. *J. Phys. Soc. Japan* **23**, 536–539 (1967)
- Krebs, J.J., Maisch, W.G.: Exchange effects in the optical absorption spectrum of Fe^{3+} in Al_2O_3 . *Phys. Rev.* **B 4**, 757–769 (1971)
- Kotlicki, A., Olsen, N.B., Olsen, J.S.: Mössbauer and X-ray study of proton radiation effects in biotite. *Radiation Effects* **28**, 1–4 (1976)
- Larsen, Jr., E.S., Gonyer, F.A., Irving, J.: Petrologic results of a study of the minerals from the tertiary volcanic rocks of the San Juan Region, Colorado. *Am. Mineral.* **22**, 898–905 (1937)
- Lehmann, G.: Ligand field and charge transfer spectra of Fe (III)-O complexes. *Z. Phys. Chem. (Frankfurt)* **72**, 279–297 (1970)
- Lehmann, G., Gudat, A.E.: Coupling between ligand field and charge transfer states in tetrahedral CoX_4^{2-} complexes. *Z. Phys. Chem. (Frankfurt)* **93**, 327–336 (1974)
- Lohr, Jr., L.L., McClure, D.S.: Optical spectra of divalent manganese salts. II. The effect of interionic coupling on absorption strength. *J. Chem. Phys.* **49**, 3516–3521 (1968)
- Low, W.: Paramagnetic resonance spectrum of manganese in single crystals of alkali halides grown from solutions. *Proc. Phys. Soc.* **69B**, 837–838 (1956)
- McClure, D.S.: Optical spectra of exchange coupled Mn^{2+} ion pairs in ZnS: MnS. *J. Chem. Phys.* **39**, 2850–2855 (1963)
- Oshima, V., Abe, H., Nagano, H., Nagusa, M.: Paramagnetic resonance of NaCl crystals containing additions of manganese impurity. *J. Chem. Phys.* **23**, 1721–1722 (1955)
- Rimsaite, J.: Studies of rock-forming micas. *Geol. Surv. Canada Bull.* 149 (1967)
- Rimsaite, J.: Structural formulae of oxidized and hydroxyl-deficient micas and decomposition of the hydroxyl group. *Contrib. Mineral. Petrol.* **25**, 225–240 (1970)
- Robbins, D.W., Strens, R.G.J.: Charge transfer in ferromagnesian silicates: The polarized electronic spectra of trioctahedral micas. *Mineral. Mag.* **38**, 551–563 (1972)
- Rossmann, G.R.: The optical spectroscopic comparison of the ferric iron tetrameric clusters in amaranthite and leucophosphite. *Am. Mineral.* **61**, 933–938 (1976)
- Smith, G.: Low temperature optical studies of metal-metal charge-transfer transitions in various minerals. *Can. Mineral.* **15**, 500–507 (1977)
- Smith, G., Strens, R.G.J.: Intervalence-transfer absorption in some silicate, oxide and phosphate minerals. *Phys. Chem. Mineral. Rocks* (R.G.J. Strens, ed.), 583–612. New York: Wiley 1976
- Stock, H.D., Lehmann, G.: Phenomena associated with diffusion of trivalent iron in amethyst quartz. *J. Phys. Chem. Solids* **38**, 243–246 (1977)
- Vedder, W.: Correlations between the infrared spectrum and chemical composition of biotite mica. *Am. Mineral.* **49**, 736–768 (1964)
- Vedder, W., Wilkins, R.W.T.: Dehydroxylation and rehydroxylation, oxidation and reduction of micas. *Am. Mineral.* **54**, 482–509 (1969)
- Wilkins, R.W.T.: The hydroxyl stretching region of the spectrum of biotite mica. *Mineral. Mag.* **36**, 325–333 (1964)
- Wilson, A.D.: Micro-determination of ferrous iron in silicate minerals by volumetric and colorimetric methods. *The Analyst* **85**, 823–827 (1960)
- Wulfsberg, C., Jones, R.B., Gray, H.B.: The structures of iron (III) in aqueous solution. *J. Am. Chem. Soc.* **89**, 3712–3720 (1967)

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