A Pink Muscovite with Reverse Pleochroism from Archer's Post, Kenya

STEVEN M. RICHARDSON

Department of Geological Sciences, Harvard University
Cambridge, Massachusetts 02138

Abstract

A pink muscovite from a manganese-bearing hydrothermal vein near Archer's Post, Kenya, has the following optical properties: \( \alpha = 1.564, \beta = 1.600, \gamma = 1.605, 2V = 41^\circ56', \) and a distinct reverse pleochroism in thick sections, with \( X = \text{rose pink}, Y = \text{pale orange-pink}, Z = \text{pale yellow}. \) The stacking polytype is \( 2M_1. \) Specific gravity = 2.89.

Mössbauer and optical absorption spectra indicate that the pink color and the reverse pleochroism are due to tetrahedral Fe\(^{3+}\) and octahedral Mn\(^{2+}\).

Introduction

Nearly all colored micas are pleochroic, usually displaying the greatest absorption of polarized light when vibration is parallel to the basal cleavage plane \( [E||(001)] \) and the least when vibration is normal to it \( [E\perp(001)]. \) Those micas in which this normal pleochroic scheme is reversed have been called "reverse pleochroic" (Faye and Hogarth, 1969).

Unlike the trioctahedral micas, reverse pleochroism in dioctahedral micas has received little mention in the mineralogical literature; an exhaustive search has yielded only one such description (Schaller and Henderson, 1926). The discovery of a second sample prompted the present study.

Observations

The Archer's Post muscovite occurs in a manganese-bearing hydrothermal vein cross-cutting Precambrian gneiss in an area five miles northeast of Archer's Post, Kenya. The general geology of the region has been mapped by Jennings (1967), but precise age relations for the hydrothermal emplacement are not known.

Associated vein minerals are braunite, spessartine, and quartz, plus minor amounts of rutile, managanapatite, oligoclase, and orthoclase. A textural study of polished thin sections suggests that quartz was a late-stage addition to the assemblage, and that the feldspars are probably wall-rock fragments. The mica comprises about 15 per cent of the hand specimens by volume.

Flakes and, where possible, books of mica were removed from the specimens and hand sorted under a petrographic microscope to obtain a sample that was optically free of inclusions. Physical and chemical determinations were made on this material.

Indices of refraction determined in white light by oil immersion are: \( \alpha = 1.564, \beta = 1.600, \) and \( \gamma = 1.605^\circ. \) The birefringence is thus 0.041. The estimated precision on indices of refraction is ±0.002. From these indices \( 2V \) may be calculated as approximately 41\(^\circ. \) An independent measurement of \( 2E, \) with appropriate corrections, yields a value for \( 2V \) of 41°56'. Distinct pleochroism was noted in thick flakes of the mica, with \( X > Y \approx Z. \) The pleochroic color scheme is \( X = \text{rose pink}, Y = \text{pale orange-pink}, Z = \text{pale yellow}. \)

The stacking polytype was determined by the relationships between percussion figures and orientation of the optic axial plane described by Deer, Howie, and Zussman (1966, p. 200). The optic axial planes of five large (0.5 cm) flakes were found to lie exactly halfway between rays of percussion figures produced on those grains, indicating the common \( 2M_1 \) polytype.

Mössbauer and optical absorption spectra indicate that the pink color and the reverse pleochroism are due to tetrahedral Fe\(^{3+}\) and octahedral Mn\(^{2+}\).

1 Mineralogical contribution No. 496, Harvard University.

2 A representative hand specimen has been deposited in the mineralogical collections of Harvard University as #110212.
measured by Westphal balance. A fairly precise value of 2.89 was thus obtained.

Wet chemical analysis of a 0.5 gram sample was performed by Dr. Jun Ito. The results of that analysis, and of a qualitative analysis for trace elements by emission spectroscopic methods, are reported in Table 1, and will be fully discussed later. A semi-quantitative analysis for fluorine was performed on two grains by electron microprobe analysis on an ARL (EMX) microprobe, operating at 8kV and using 1.5 nA sample current to minimize sample volatilization. No significant counts above background were detected, and thus fluorine content in the mica is assumed to be very low or non-existent.

A 2 mm thick book of muscovite was mounted in epoxy, and a thin section perpendicular to (001) was prepared from it for optical absorption spectrography. In order to accentuate the pleochroism in the $E|| (001)$ and $E \perp (001)$ directions, the section was ground to an arbitrary thickness of 0.42 mm, approximately 14 times the thickness of a standard thin section. Spectra were obtained in plane polarized light with $E|| (001)$ and $E \perp (001)$ at room temperature on a Cary 17 recording spectrophotometer, in the manner described by Burns (1966). The polarizers in both the sample and reference beams were Nicol prisms, allowing the measurement of fully polarized spectra at frequencies well into the infrared region (25000-5000 cm$^{-1}$).

The oxidation state and coordination of iron in the muscovite were investigated by Mössbauer spectroscopy at room temperature, using metallic iron as the standard absorber. The powdered sample was irradiated by a cobalt-57 source in palladium driven at constant acceleration, and the transmitted radiation was detected by a Reuter-Stokes gas-filled proportional counter (97% Kr - 3% CO$_2$). Output was displayed through a 1024-channel pulse-height analyzer operating in symmetric sawtooth velocity mode. The spectrometer was arranged to allow two experiments to be performed simultaneously with two cobalt-57 sources on opposite ends of the vibrator, so that data from only one half of the output channels were computed to give the spectrum in Figure 1. Lorentzian line shapes were fitted to the data on the joint MIT-Harvard IBM 370/65 computer using the program written by Stone (1967).

### Results

#### Chemical Analyses

The wet chemical analysis of the Archer’s Post muscovite is compared in Table 1 to that reported by Schaller and Henderson (1926) for the reverse pleochroic Pilar muscovite. No quantitative determination of the manganese oxidation state was performed on the Archer’s Post sample. Total manganese is reported here as Mn$_2$O$_3$, however, following the assumption made by Heinrich and Levinson (1953). The wet chemical analysis and the Mössbauer spectra both indicate that iron is present only

<table>
<thead>
<tr>
<th>Element</th>
<th>Archer’s Post</th>
<th>Pilar, N.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.10</td>
<td>45.16</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>34.60</td>
<td>35.61</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.81</td>
<td>2.95</td>
</tr>
<tr>
<td>FeO</td>
<td>&lt; 0.1</td>
<td>-</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>0.55***</td>
<td>0.70</td>
</tr>
<tr>
<td>MgO</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>BaO</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.21</td>
<td>1.03</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>10.8</td>
<td>10.32</td>
</tr>
<tr>
<td>Rb$_2$O</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>4.85</td>
<td>4.36</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>O=P</td>
<td>99.94</td>
<td>100.18</td>
</tr>
<tr>
<td>Total</td>
<td>99.94</td>
<td>100.16</td>
</tr>
</tbody>
</table>

* Jun Ito, analyst. Emission spectroscopic analysis also indicates trace amounts of Ga, Be, Sr, Pb, Ag, and V.
* From Schaller and Henderson (1926). E. P. Henderson, analyst.
* All manganese recalculated as Mn$_2$O$_3$. See text.
as Fe³⁺ in the sample; and since manganese is more easily oxidized than iron, I assume that it also is present only in the trivalent state.

The major substitutional impurities in the Archer's Post sample are Ti, Fe³⁺, Mn³⁺, and Mg. Of these, neither titanium nor magnesium occurs in the Pilar muscovite, and thus they cannot be invoked to provide a common explanation for the color or pleochroism of the two micas. In other respects the two muscovites are chemically similar. There is little solid solution toward paragonite or phengite in either; Mn³⁺/Fe³⁺ ratios are similar and low in both; and both are low or deficient in lithium, rubidium, and fluorine.

**Mössbauer Spectrum**

Computer analysis of the Mössbauer spectrum was first attempted by assuming that the spectrum could be described by one doublet, as suggested qualitatively by a plot of the raw data. Intensities and line widths of both peaks were constrained to be equal. A chi-squared value of 536 indicates a high degree of confidence for this initial fit, and no significant improvement in chi-squared was produced in a second trial fit with no constraints on either line width or intensity. Attempts to fit more than two peaks to the raw data were unsuccessful. The initial fit (Fig. 1) is therefore taken to be the best one. Quadrupole splitting and isomer shift relative to the metallic iron standard absorber are 0.73 mm/sec and 0.46 mm/sec respectively. The line widths at half peak height are 0.82 mm/sec. The value for quadrupole splitting is in good agreement with that found by Brown and Pritchard (1969) for ferric iron in orthoclase, substantiating the results of the wet chemical analysis in Table 1. No ferrous iron was detected in this specimen.

Assignment of a coordination number for the Fe³⁺ ion on the basis of the Mössbauer data alone, however, is less certain. The isomer shift reported here is nearly identical to that reported by Brown and Pritchard and attributed to tetrahedral coordination. Other studies by Weaver, Wampler, and Pecuil (1967), Hogarth, Brown, and Pritchard (1970), and Annersten (1974), however, indicate that isomer shifts for tetrahedral Fe³⁺ in phyllosilicates are generally much smaller than in ferriorthoclase. Without the strong supportive evidence of the optical absorption spectra discussed below, therefore, it would be difficult to assert that iron in the Archer's Post muscovite is tetrahedrally coordinated. No explanation is offered for the ambiguous isomer shift, other than a repetition of Brown and Pritchard's warning that Mössbauer spectra do not always provide a wholly reliable measure of coordination when considered alone.

**Optical Absorption Spectra**

In Figure 2 the upper absorption curve, obtained with \( E_{\perp} \) (001), is dominated by major absorption peaks at 19608 cm⁻¹ and 22624 cm⁻¹. A number of smaller peaks occur between 20700 cm⁻¹ and 22600 cm⁻¹, and intense ultraviolet absorption occurs beyond about 26300 cm⁻¹. The spectrum is identical in almost all respects with the unpolarized spectrum of a pink muscovite from Sogn, Norway, reported recently by Askvik (1972). Reverse pleochroic ferri-phlogopites investigated by Faye and Hogarth (1969) also have similar absorption peaks at 19200 cm⁻¹ and 22700 cm⁻¹, described by them as spin-forbidden \( d-d \) bands of tetrahedral Fe³⁺. Studies of iron-bearing garnets (Manning, 1972) and ferri-orthoclase (Grum-Grzhimailo and Rimskaya-Korsakova, 1964; Faye, 1969) also as-
sign to tetrahedral ferric iron: the absorption peaks between 20300 cm⁻¹ and 22700 cm⁻¹ and in the near ultraviolet spectrum.

In contrast, the lower curve on Figure 2, produced with \( E_\perp \text{(001)} \), exhibits only two peaks in the range from 20300 to 22700 cm⁻¹, both greatly reduced in intensity from the \( E_\parallel \text{(001)} \) spectrum. The major absorption peak at 19608 cm⁻¹ is almost completely absent, apparently overwhelmed by a major broad peak centered at 18018 cm⁻¹. Similar bands in epidote spectra at 18000 cm⁻¹ (Burns and Strens, 1967) and in tourmaline at 18400 cm⁻¹ (Manning, 1973) have been assigned to octahedrally coordinated Mn³⁺, and a similar assignment is also suggested here. The broad weak absorption band around 13700 cm⁻¹ may also be due to octahedral Mn³⁺, again by analogy with Mn³⁺ spectra in tourmaline (Manning, 1973). Other major trivalent manganese peaks measured with 22700 cm⁻¹ and 21300 cm⁻¹ by Manning and at 22000 cm⁻¹ by Burns and Strens, if present, are probably masked by the absorption peaks of Fe³⁺ in that region.

If some or all of the manganese were divalent, rather than trivalent as assumed earlier, absorption peaks for Mn²⁺ should be expected at 24000, 23200, and 18500 cm⁻¹ by analogy with manganoan lepidolite spectra (Faye, 1968). These are spin-forbidden transitions in Mn²⁺, however, and are predicted to be weak. The higher-frequency absorption bands may, of course, be present in the spectra presented here, but overwhelmed by the greater intensity of ferric iron absorption bands. The 18500 cm⁻¹ band, shifted to slightly longer wavelengths, might be the 18018 cm⁻¹ peak assigned earlier to Mn³⁺. Considering the nearly identical structures of lepidolite and muscovite, such a shift seems somewhat unlikely, however. For this reason, and for the geochemical reasons mentioned earlier, therefore, it seems most likely that Mn³⁺ is the major manganese species affecting optical absorption in the Archer’s Post muscovite.

It is therefore suggested that light polarized perpendicular to the basal cleavage is predominantly absorbed in the blue-green and ultraviolet by interaction with ferric iron in tetrahedral coordination. White light polarized parallel to the basal plane in the Archer’s Post muscovite is also affected by interaction with tetrahedral Fe³⁺, but experiences additional absorption at longer wavelengths because of octahedral Mn³⁺. The crystal field effects of other substitutional impurities are negligible. The reverse pleochroic effect is clearly due to differences in the absorption intensity arising from ferric iron interactions in the two polarization directions.

**Discussion**

Color in muscovites has been the subject of much discussion in the mineralogical literature. Specifically, pink hues have been attributed to the presence of copper and lead (Iimori and Yoshimura, 1929), fluorine (Micke, 1950), titanium (Webb, 1939; Ödman, 1950; Rimšaite, 1967), lithium (Ellis, 1950), manganese (Bowman, 1902; Meixner, 1939; Faye, 1968; Meinhold and Frisch, 1970; and others), ferric iron (Melankholin, 1948; Van der Plas, 1959; Finch, 1963; Faye, 1968), and the combined presence of ferric iron and manganese (Schaller and Henderson, 1926; Shibata, 1952; Heinrich and Levinson, 1953, 1955; Aspvik, 1972; and others). A review of published analyses of pink muscovites, including analyses performed since the review of Heinrich and Levinson (1953), confirms their observation that both manganese and iron are present in the vast majority of pink muscovites, and iron is common to all.

The results of spectroscopic studies by Finch (1963), Rimšaite (1967), and Faye (1968), however, indicate that although Mn³⁺ is frequently a chromophore in muscovite, as in several other silicates (Burns and Strens, 1967; Petrusenko and Padera, 1970; Volchenko, 1971; and others), it is not the primary coloring agent in a large number of pink muscovites. Iron, rather than manganese,
appears to be the common contributor to the absorption spectra of pink muscovites for which data are currently available.

These same studies indicate, however, that there is no correlation between absolute or relative iron content and either hue or absorption intensity in pink muscovites. Even a cursory search of published muscovite analyses easily reinforces the truth of this interpretation: there is indeed a great number of pale to colorless iron- and manganese-bearing muscovites. The implication is clearly, as Finch (1963) pointed out, that the structural environment and resulting crystal field effects of iron have the most universal influence on “pinkness” in muscovite.

Structural variations and associated changes in site occupancy are well documented for the dioctahedral micas. Güven and Burnham (1967), for example, have shown that a slight ordering of tetrahedral aluminum and silicon occurs in muscovite with the 3T stacking sequence. Similar ordering of tetrahedral cations, as well as a distortion of the tetrahedral sheet relative to that in end-member muscovite, has been reported in phengites by Güven (1967, 1971). As far as I am aware, however, these structural variations or others like them have not been shown to correlate with a color change in any mica. In fact, even if such a correlation could be shown, it would not explain the pink color of the Archer’s Post mica, which is a nearly pure end-member 2M₄ muscovite.

A tentative hypothesis suggested by the results of Askvik (1972) and the present study is that pink color in muscovite results from substitution of ferric iron for silicon or aluminum in tetrahedral sites. Certainly the color in both the Archer’s Post mica and Askvik’s mica from Sogn results primarily from tetrahedral ferric iron, as can be seen from the published spectra. More convincingly, the great volume of spectroscopic work performed by Finch (1963) shows consistent absorption maxima, which have been assigned earlier in this paper to tetrahedral Fe³⁺, at 22570 cm⁻¹ and 19685 cm⁻¹ in the spectra of all of the pink muscovites analyzed. Possible additional support for this view is provided by the deep red color of cronstedtite, a sheet silicate known to have half of its tetrahedral sites filled with ferric iron (Gossner, 1935; Hendricks, 1939).

This suggestion has the advantage, not offered by the other structural hypotheses just presented, of explaining the lack of correlation between iron content and color. Regardless of the total iron content or even the Fe³⁺ content reported in the chemical analysis, pink color in muscovite, according to this view, depends in intensity only on the amount of Fe³⁺ in the tetrahedral layer. Mn⁴⁺, although it contributes to the spectra of the Archer’s Post and Sogn muscovites and undoubtedly of a large number of muscovites classified as “rose muscovites” by Heinrich and Levinson (1953), is probably not the major source of pink hues in most muscovites.

Summary and Conclusions

The present study shows that reverse pleochroism in muscovites results from tetrahedral ferric iron, probably by the mechanism originally proposed for phlogopites (Faye and Hogarth, 1969; Hogarth et al, 1970). Presumably the same correlation between tetrahedral iron content and pleochroism can be made for muscovite that Hogarth et al (1970) found for phlogopite: “the correlation between the amount of tetrahedral ferric iron and biabsorbance is qualitatively good, the normally pleochroic micas being those with the least amount of Fe³⁺ and the reverse ones having the most.” This relationship has been well established in synthetic phlogopites (Hazen and Wones, 1972; Hazen, private communication, 1973) as well as in the natural materials discussed by Hogarth et al, establishing a firm basis for similar expectations in muscovites.

This work suggests further that tetrahedral Fe³⁺ is the major chromophore in pink muscovites. If this hypothesis is valid, then many pink muscovites should also be reverse pleochroic, and all reverse pleochroic muscovites should be pink. This test remains to be performed on a statistically significant sample of micas, but if substantiated should constitute a valuable petrologic tool.

The lack of attention to reverse pleochroic muscovites, pink or not, in the mineralogical literature is not as discouraging to these hypotheses as it might seem at first glance. As noted earlier in this paper, the Archer’s Post mica, though highly colored, shows its strong pleochroism only in sections several times the thickness of a standard thin section. Since micas are rarely examined in transverse section except in standard thin sections, it is not hard to believe that a great many reverse pleochroic muscovites may have gone unrecognized by petrographers.

Acknowledgments

The author is grateful to Dr. John Saul of Nairobi, Kenya, who provided the specimens from Archer’s Post. Thanks are also due to Dr. Cornelius Hurlbut, who called the author’s attention to the mineral assemblage and its
intriguing mica. Dr. Roger Burns provided essential aid in the performance and interpretation of the spectroscopic work. The personal observations and comments of Drs. Charles W. Burnham, Thomas Shankland, and James B. Thompson are also greatly appreciated.

References


———, and CHARLES W. BURNHAM (1967) The crystal structure of 3T muscovite. Z. Kristallogr. 125, 163–183.


Manuscript received, June 21, 1974; accepted for publication, August 30, 1974.