More data on red muscovite

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Abstract

Red-tinted muscovite from Precambrian metamorphic rocks of New Mexico, showing normal pleochroism, coexists with piemontite, viridine (manganian andalusite), and hematite, in contrast to white mica that coexists with magnetite and zoisite. Red muscovite is higher in Mn and Cu, but lower in Cr, than adjacent green to white muscovite. High concentrations of Mn in green-tinted pegmatitic muscovite suggest that oxidation state of Mn, rather than absolute concentration, accounts for the red tint. Both Mn^{3+} and Cu^{2+} gain crystal-field stabilization energy in distorted octahedral sites. Our data support the conclusion that Mn^{3+} is probably the main chromophore of pink-to-red muscovite, but we do not rule out the thesis that Fe^{3+} in tetrahedral sites may cause reverse pleochroism in dioctahedral micas.

Introduction

Richardson (1975) described reverse pleochroism in a pink muscovite from Kenya and attributed the color to ferric iron in tetrahedral sites. He generalized his conclusions with the suggestion that tetrahedral Fe^{3+} may be the major chromophore of all pink muscovite. Annersten and Hålenius (1976) challenged this generalization and also questioned specific details of Richardson's interpretation of his data from the Kenyan specimen. They concluded that Mn^{3+} in octahedral coordination is the most likely chromophore of pink muscovite, which is a reaffirmation of a view expressed in earlier investigations. In his reply, Richardson (1976) recognized that Annersten and Hålenius had raised serious objections to his interpretation, and he expressed the need for more information to further evaluate the situation.

Richardson (1975) cited Schaller and Henderson's (1926) description of "purple" muscovite from Pilar, New Mexico, as the only other reported occurrence of reverse-pleochroic dioctahedral mica in the literature. We investigated the geochemistry of micas from northern New Mexico (Gresens and Stensrud, 1974b), including samples of pinkish to reddish muscovite collected near one of Schaller and Henderson's localities.

The purpose of this report is (1) to describe additional occurrences of red muscovite, (2) to comment on the significance of our specimens with respect to the dispute between Richardson and Annersten/ Hålenius, and (3) to present new observations on the geochemistry of red muscovite.

Geologic setting

Most of our work was done in two separated Precambrian terranes (Fig. 1): (1) the Picuris Range south of Taos, New Mexico, and (2) the Las Tablas quadrangle. Red muscovite occurs in both areas. Additional specimens of red muscovite were collected from roadcuts at Red River Pass (Fig. 1). Red muscovite occurs as mappable zones in feldspathic schist and quartz–muscovite schist (both derived from metarhyolite) in amphibolite-grade metamorphic rocks in the two main study areas (Gresens and Stensrud, 1974a, b). Maps showing their locations are published in Gresens and Stensrud (1974a).

In the Las Tablas quadrangle, we mapped thin, discontinuous zones composed of alternating layers
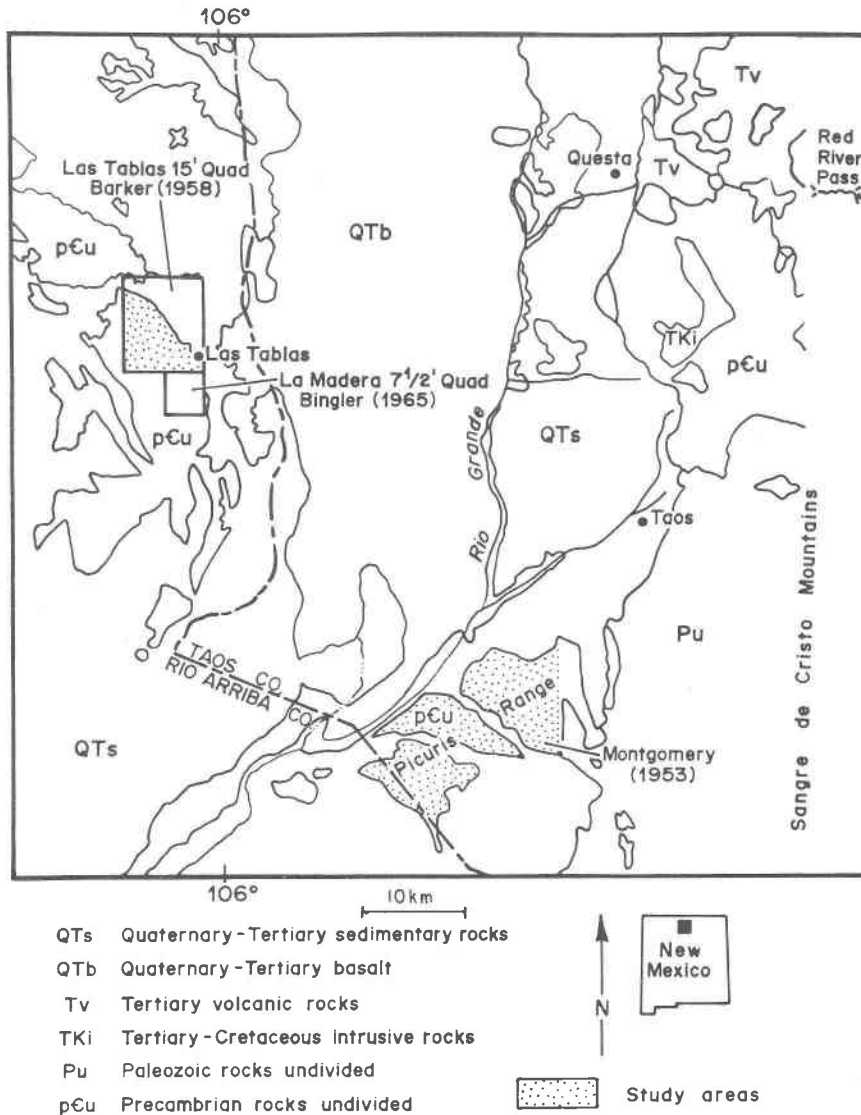
Fig. 1. Index map of New Mexico showing location of the Las Tablas area, the Picuris Range, and Red River Pass. References to publications containing general geologic maps of the areas are given on the index map.

of (1) pinkish to reddish schist with red muscovite and (2) greenish-gray schist with normal white to pale green muscovite. There are no textural differences between the two types of schist. Mineralogically, there are only two significant distinctions between the two types of schist: (1) reddish schist contains piemontite (Mn–epidote), whereas silvery to greenish-gray schist contains green zoisite if an epidote mineral is present; (2) the accessory opaque oxide in greenish-gray schist is magnetite, whereas the opaque oxide in reddish schist is a non-magnetic mineral, presumably hematite. Hematite coexists with pie-

montite in nearby rocks (Stensrud and Gresens, 1973). Although muscovite-rich quartzofeldspathic pegmatites are abundant in the area, red muscovite was not observed in them.

The occurrences of red muscovite in the Picuris Range are similar to those in the Las Tablas quadrangle, except that there is little feldspathic schist present, because most of the metarhyolite has been metasomatically altered to quartz–muscovite schist (Gresens and Stensrud, 1974a, b). Metamorphism has reached staurolite grade in the overlying Ortega Quartzite. One sample of reddish schist contains viri-

dine (manganian andalusite) coexisting with hematite (Stensrud and Gresens, 1972). The locality described by Schaller and Henderson (1926) must be very near our sampling localities. Although the quartzo-feldspathic pegmatites we observed here did not contain their cited occurrence of "purple" muscovite, we have seen similar occurrences at Red River Pass.

Secondary shearing, brecciation, and hydrothermal alteration have blurred the primary geologic relationships at Red River Pass. Nevertheless, it is clear that there is a patchy development of pegmatitic "pockets' in feldspathic gneiss. The grain size is much coarser in these patches, and there is a higher quartz/feldspar ratio due to development of muscovite at the expense of microcline. In some rocks, the pegmatitic patches contain normal green muscovite, but others contain large (up to 2.5 cm) books of red muscovite. The color is often a bronze red, apparently similar to the pegmatitic occurrences described by Schaller and Henderson (1926). Piemontite was not observed in thin sections of these specimens.

Pleochroism

Several of the most strongly-colored red muscovite specimens were examined in thin section, including samples from the Pilar locality, the Las Tablas area, and Red River Pass. All have normal pleochroism. Moreover, in contrast to Richardson's (1975) statement, the pleochroic formula given by Schaller and Henderson (1926) is for normal, not reverse, pleochroism. We conclude that all the pink to red muscovite from northern New Mexico has normal pleochroism and that Richardson's Kenyan specimen is the only known example of a reverse-pleochroic dioctahedral muscovite.

Analytical results

A general report on the geochemistry of muscovite from northern New Mexico is already published (Gresens and Stensrud, 1974b), and the complete set of analyses is available in NAPS document #02419 (see footnote, p. 1581 of the above citation, for details). The mean chemical compositions of red muscovites and non-red muscovites from northern New Mexico are compared in Table 1. For most elements, red muscovite composition is not significantly different from the composition of other schist-derived muscovite. The significant differences are in the higher Mn, Cu, and Zn, and lower Cr values for red muscovite. Our mean composition for red muscovite is not significantly different from other reported analyses (Annersten and Hålenius, 1976, Table 1).

At several localities, we sampled both reddish schist and adjacent greenish-gray schist. The distance between pairs in each set varied, but most were collected within 3 meters of each other and many were within 1 meter (Table 2). Chemical data for these samples are plotted in Fig. 2, emphasizing the strong enrichment of Mn and Cu in red muscovite and the depletion in Cr.

Discussion

We followed Richardson (1975) and Annersten and Hålenius (1976) in reporting the Fe content of red muscovite as Fe_2O_3 and the Mn content as Mn_2O_3 (Table 1). This differs from our earlier report (Gresens and Stensrud, 1974b), in which we simply reported total Fe and Mn as the elements. Richardson assumed that Mn is trivalent because Mössbauer spectra indicated that Fe is all ferric and "manganese is more easily oxidized than iron." This line of reasoning is probably not valid. At 25°C and 1 atm, Fe_3O_4 oxidizes to Fe_2O_3 at $PO_2 = 10^{-68.2}$, but MnO does not oxidize to Mn_2O_3 until $PO_2 = 10^{-56.8}$. In solution, at 25°C and 1 atm, the standard potential for $Fe^{2+} \rightarrow Fe^{3+} + e^-$ is 0.77 volts, whereas the standard potential for $Mn^{2+} \rightarrow Mn^{3+} + e^-$ is higher at 1.51 volts (Heinrich and Levinson, 1953). However, Annersten and Hålenius also assigned a trivalent state for Mn in their specimens of pink muscovite, on the basis that EPR measurements showed no reasonance spectra ascribable to Mn^{2+}, whereas optical spectra showed absorption bands of Mn^{3+}. Mössbauer measurements by Annersten and Hålenius also confirmed that Fe is all trivalent. It seems safe to assume that Mn and Fe are predominantly trivalent in the New Mexico specimens. For the sake of comparison, Fe and Mn concentrations in white to green muscovite are reported as trivalent oxides in Table 1, although this is probably not strictly true.

We had suspected Mn^{3+} as the chromophore in the New Mexico specimens for several reasons. (1) The red muscovite coexists with piemontite and viridine; in both of these minerals the chromophore is known to be Mn^{3+} (Burns, 1970). In piemontite, Mn^{3+} in distorted octahedral sites gives rise to the red color. (2) Although the red muscovite shows a definite enrichment in total Mn relative to "normal" muscovite (Table 1 and Fig. 2), many pegmatitic muscovites from the same area have equal or greater amounts of total Mn, but are colored green. Thus, although Mn is clearly a factor, the absolute Mn concentration is not the total control of color, suggesting that the valence state is important. (3) The presence of mag-

Table 1. Mean* and variation** of the compositions of groups[†] of muscovite specimens

Element (wt.% or PPM)	Red muscovite	Green to white muscovite			Pegmatite	All non-reddish schist (comb. L,U,P)[††]
		L	U	P		
SiO_2 %	44.15					45.02
TiO_2	1.2 (0.2 – 1.8)	1.2 (0.1 – 2.0)	0.5 (0.1 – 1.0)	0.8 (0.3 – 2.0)	0.5 (0.2 – 1.2)	1.0
Al_2O_3	31.4 (± 2.1)	30.8 (± 2.5)	35.7 (± 2.5)	31.0 (± 3.0)	32.1 (± 4.0)	31.1
Fe_2O_3	5.4 (± 0.6)	5.4 (± 0.7)	3.7 (± 1.4)	4.6 (± 1.1)	3.1 (± 1.3)	4.8
Mn_2O_3	0.34 (0.09 – 0.68)	0.18 (0.04 – 0.49)	0.30 (0.03 – 0.62)	0.07 (0.01 – 0.14)	0.06 (<0.01 – 0.16)	0.12
MgO	0.68 (0.05 – 2.06)	1.28 (0.05 – 2.82)	0.20 (<0.02 – 0.53)	1.48 (0.36 – 2.19)	0.61 (0.08 – 2.65)	1.15
Na_2O	0.40 (0.31 – 0.81)	0.37 (0.26 – 0.93)	0.57 (0.40 – 1.74)	0.47 (0.27 – 1.46)	0.76 (0.30 – 2.21)	0.48
K_2O	10.42					10.17
F	0.09					0.18
Li PPM	97 (20 – 140)	168 (20 – 880)	212 (25 – 610)	57 (<10 – 150)	59 (<10 – 220)	128
Rb	323 (150 – 550)	353 (40 – 820)	1183 (310 – 3400)	253 (190 – 310)	256 (90 – 410)	317
Ba	2000					1900
Zn	478 (40 – 1040)	396 (70 – 1400)	744 (100 – 1300)	95 (30 – 230)	81 (<10 – 190)	283
Cu	170 (<20 – 460)	36 (<20 – 500)	28 (<20 – 35)	30 (<20 – 110)	26 (<20 – 60)	33
Cr	24 (<10 – 70)	72 (<10 – 360)	19 (<10 – 130)	131 (10 – 250)	76 (<10 – 300)	81

* Mean is based on atomic absorption analyses of 18 red muscovites, 99 L muscovites, 21 U muscovites, 36 P muscovites, and 15 pegmatite muscovites for Ti, Al, Fe, Mn, Mg, Na, Li, Rb, Zn, Cu, and Cr. Mean is based on electron microprobe analyses of 6 red muscovites and 24 non-red muscovites (L, U, and P) for Si, K, F, and Ba.

** For major elements determined by AA analysis (Al, Fe), the standard deviation reported here (± value in parentheses) is a measure of the variation of their concentrations among the samples in the group; it is not analytical precision. For other elements determined by AA analysis, the values in parentheses are the range, i.e., the highest and lowest observed values in each group of samples. Analytical precision for individual analyses is reported in Gresens and Stensrud (1974b, table 2).

† Red muscovites are all from metarhyolitic quartz-muscovite schist from both study areas. L muscovites are from metarhyolitic quartz-muscovite schist in the Las Tablas area. U muscovites are from metasedimentary rocks in the Las Tablas area. P muscovites are a mixture of metasedimentary and metarhyolitic muscovite from the Picuris Range. Pegmatite muscovites are from both study areas.

†† This column combines the means for L, U, and P samples (weighted according to the number of samples per group) for comparison with the overall mean composition of red muscovites from both study areas.

netite in greenish-gray schist but hematite in reddish schist confirms that at least the oxidation state of Fe differs, and probably the oxidation state of Mn differs between the two types of schist.

We agree with Annersten and Hålenius that Mn^{3+} in distorted octahedral sites is the likely chromophore of red muscovite; our observations are in complete accord. It is possible that Richardson (1975) is correct in ascribing the reverse pleochroism to Fe^{3+} in tetrahedral sites; but, as noted above, his specimen appears to be the only reported example of reverse pleochroism in a dioctahedral mica.

Assuming that Mn^{3+} in distorted octahedral sites is the cause of color in the New Mexico specimens, the enrichment of Cu in red muscovite is explained by crystal-field theory (Burns, 1970). Stabilization of Mn^{3+} is brought about by Jahn-Teller splitting of the energy levels of the d-orbitals in distorted sites; the electronic configuration of Mn^{3+} permits an additional crystal-field stabilization energy (CFSE). Cu^{2+} is another ion that gains CFSE in octahedral sites because of the Jahn-Teller effect. The enrichment of Cu in red muscovite (Table 1 and Fig. 2) may result from several factors: (1) the higher oxidation state of the reddish schists may have produced a higher ratio of divalent to univalent Cu in reddish schist than in greenish-gray schist; and (2) the spontaneous distortion of octahedral sites due to the presence of Mn^{3+} (Burns, 1970, sec. 6.3) may have provided additional sites that could stabilize Cu^{2+}.

The low Cr concentrations in red muscovite (Table 1 and Fig. 2) are surprising in view of the existence of fuchsite, a variety of muscovite that may contain up to 6 percent Cr_2O_3 (Deer *et al.*, 1962). It seems unlikely that oxidation of Cr to the next highest state, Cr^{6+}, in reddish schist could be invoked to explain the phenomenon. Selected whole-rock analyses showed no significant differences between reddish schist and greenish schist for a number of elements;

Table 2. Distance between pairs or sets of red and non-red muscovite samples

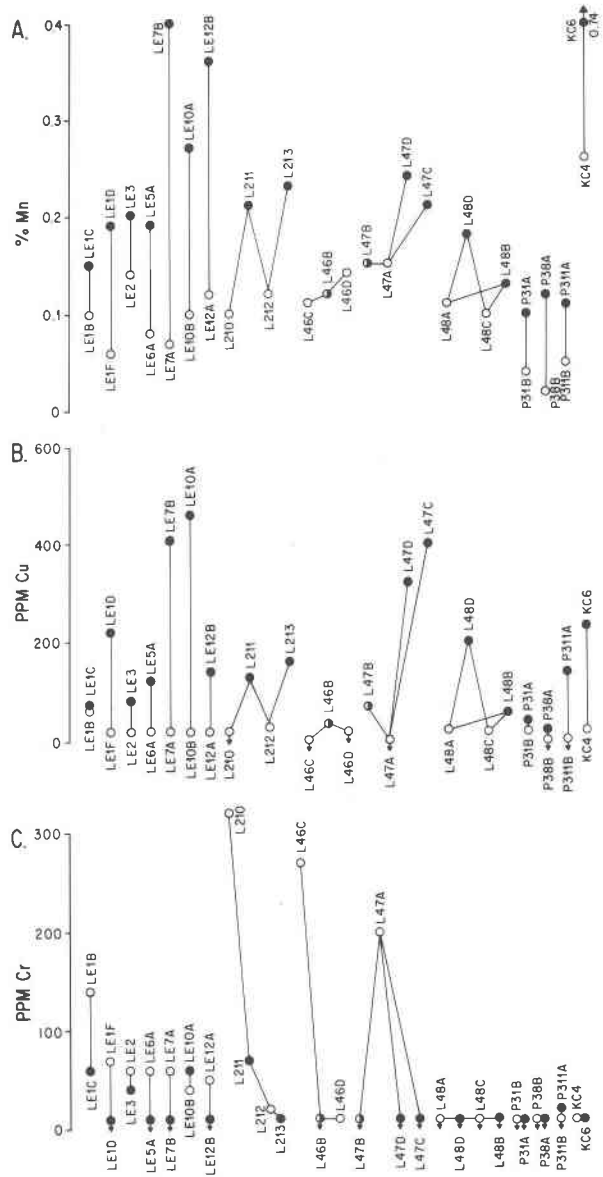| Sample number		Distance (meters)
Red or pink muscovite	Green to white muscovite	
LE1C	LE1B	2.5
LE1D	LE1F	<3
LE3	LE2	9
LE5A	LE6A	<3
LE7B	LE7A	0.6
LE10A	LE10B	9
LE12B	LE12A	1.5
L211	L210	95
L211	L212	9
L213	L212	<1
L46B	{ L46C	<1.5
	{ L46D	18
L47B } L47C }	L47A	<3
L47D	L47A	43
L48B	{ L48A	<2
	{ L48C	
L48D	{ L48A	12
	{ L48C	
P31A	P31B	<1
P38A	P38B	<1
P311A	P311B	<1
KC6	KC4	190

Fig. 2. Plots of concentrations of Mn (A), Cu (B), and Cr (C) in pairs or sets of adjacent red and non-red muscovite specimens. Horizontal scale has no quantitative significance. Distances between pairs or members of sets are given in Table 2. Solid dots are red muscovite; open circles are non-red muscovite. Half-solid dots are very pale pink muscovite. Arrows pointing down signify values less than the value of the circle or dot (below the analytical detection limit). Arrow pointing up on diagram (A) denotes a value too high to be included quantitatively. The "L" prefix denotes Las Tables area; the "P" prefix denotes Picuris Range. All data are based on atomic absorption analyses except for the KC4-KC6 pair, which plots emission spectrographic data from an additional pair of specimens from the Las Tablas area, taken from Gresens (1967).

however, Cr concentrations were below the detection limit for whole-rock analyses. Therefore a remote possibility remains that the difference in Cr concentrations of red and "normal" muscovite reflect original compositional differences in the two types of schist. In an earlier study, Gresens (1967) noted high concentrations of Cr (500–1170 ppm) in accessory opaque oxide minerals from similar greenish-gray schist from the Las Tablas area. A possibility (which was not part of our investigation of muscovite geochemistry) is that the difference in oxide mineralogy between the two schist types favors a higher partitioning of Cr toward the oxide phase in reddish schists. We know of no way to explain the differences in Cr concentration by crystal-field effects.

Although an apparent higher average concentration of Zn in red muscovite is suggested by Table 1, the statistics may be misleading for this element. For example, it should be noted that the concentration of Zn in normal muscovite from some schists (L group, Table 1) is nearly as high as Zn concentration in red muscovite. In contrast to Mn, Cu, and Cr, Zn showed no consistent preferences for either red muscovite or normal muscovite in plots analogous to those in Fig. 2. Crystal-field theory does not predict any increase in CFSE of Zn^{2+} because of the Jahn-Teller effect.

An interesting sidelight is the geochemical behavior of very pale pink muscovite in a terrane where most of the red muscovite is a much deeper shade. Figure 2a shows that even though the pink color is beginning to show, the Mn concentration is no greater than the concentration in adjacent white muscovite. However, the pale pink specimens do begin to show an enrichment in Cu (Fig. 2b) and an avoidance of Cr (Fig. 2c).

In summary, our data strongly support the conclusion of Annersten and Hålenius that the usual chromophore of red and pink muscovite is Mn^{3+} in distorted octahedral sites. However, we do not rule out the possibility that Fe^{3+} in tetrahedral sites may be the cause of reverse pleochroism in dioctahedral micas, as Richardson suggested for his Kenyan specimen.

Appendix

Accessible localities of schist bearing red to pink muscovite and piemontite

Las Tablas area. Refer to U. S. Geological Survey 7.5-min. topographic map series, Las Tablas, New Mexico, N3530-W10600/7.5 (1963).

A NW-trending band of reddish schist is exposed at or near the bottom of Spring Creek in section 3, T27N, R8E. Accessible by walking about 2 km down Spring Creek from its intersection with State Road 111 in the SW corner of section 33, T28N, R8E. A N- to NW-trending band of reddish schist crosses Kiowa Canyon in the southern part of section 11, T27N, R8E, about 0.5 km west of the border between sections 11 and 12. Accessible by taking a jeep trail from Poso Lake in section 15, T27N, R8E to its intersection with Kiowa Canyon in the SW corner of section 11 and walking about 1 km east down Kiowa Canyon. A N-trending band of reddish schist crosses a forest road 100 meters east of a 3-way junction of forest roads in the SW quadrant of section 24, T27N, R8E. This is the most accessible locality in the Las Tablas quadrangle because it can be reached directly by a passenger vehicle. The best exposures of reddish schist are south of the intersection of the band with the forest road.

Picuris Range. Refer to U. S. Geological Survey 7.5-min. topographic map series, Carson, New Mexico, N3615-W10545/7.5 (1961).

NE-trending bands of reddish schist interlayered with greenish or silvery schist are intersected along a N- to NW-trending ridge that juts out toward the Rio Grande River in the middle southern border of section 32, T24N, R11E. Accessible by driving 0.7 km SE from the town of Pilar on U.S. highway 64 and climbing the steep cliffs to the south.

Red River Pass. Refer to U.S. Geological Survey 7.5-min. topographic map series, Red River Pass, New Mexico, N3637.5-W10515/7.5 (1963).

Localities are in an unsurveyed portion of the map. From Bobcat Pass on State Highway 38 (Taos County–Colfax County Line), a roadcut containing red muscovite is located 2.6 km south and east on Highway 38. A second roadcut is located 2.4 km further south.

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