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PETROCHEMICAL INVESTIGATION OF THE SHADOW LAKE PIEMONTITE ZONE, EASTERN SIERRA NEVADA, CALIFORNIA

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ABSTRACT. The Shadow Lake piemontite zone is located within the Jurassic to Triassic metavolcanic and metasedimentary units of the Ritter Range roof pendant in the eastern Sierra Nevada. The piemontite-bearing schists are dominantly pyroclastic in origin (tuffs, ashflows, minor chert), of dacitic to rhyodacitic composition, and constitute a long, narrow (6 km × 30 meters) northwest-southeast trending zone sandwiched between green epidote-rich, more mafic (andesitic to basaltic) tuffs and flows. An extended cycle of pre- to post-tectonic crystallization under conditions transitional between the greenschist and epidote–amphibolite facies resulted in mineral assemblages unusual for low grade metavolcanic rocks: quartz + albite + phengitic muscovite + phlogopite + tremolite + hematite ± clinochlore ± spessartine. Whereas the majority of the Ritter Range strata contain abundant pods and veins of yellow-green epidote, the Shadow Lake tuffs are distinguished by sporadic development of piemontite, absence of epidote, and greater concentrations of fine-grained disseminated hematite.

Chemical and petrographic study involved examination of the relationship between crystal chemistry and mineral stability in an attempt to explain the occurrence of piemontite within these units. Whole rock chemical analyses indicate that the piemontite–bearing schists, although distinguished by a variety of Mn-rich minerals, are similar in Mn-content to "normal" metavolcanic rocks and to the adjacent epidote–bearing units. Unusually Mg-rich compositions and high Mn/Fe ratios for coexisting micaceous phases and tremolite indicate formation under conditions of high oxygen fugacity, as supported by theoretical and experimental evidence. Cation partitioning suggests that more oxidizing fluid compositions may have stabilized piemontite in these crystal tuffs rather than the more usual epidote or Mn-garnet. The high f_{O_2} conditions may have been established during devitrification of the fine-grained glassy, tuffaceous matrix to quartz + feldspar + hematite. The presence of abundant hematite maintained high f_{O_2} and effectively immobilized much of the iron throughout subsequent metamorphism.

INTRODUCTION

Although not a common rock-forming mineral, piemontite has attracted considerable interest in the geological literature for several reasons: its affinity to the geologically important epidotes, its sporadic occurrence within a wide range of metamorphic environments, and its striking characteristic color and pleochroism. More important, the incorporation into piemontite's structure of two transition metals, Fe and Mn, makes it an ideal mineral for examining the relationship between crystal chemistry and mineral stability in multivalence equilibria.

The development of piemontite must require an unusual metamorphic environment; moderately Mn-rich metamorphosed pelitic and psammitic rocks, metavolcanics, and metacherts such as those in which piemontite occurs would more commonly incorporate Mn into minerals such as green epidote or spessartine garnet. The presence of Mn^{+3} in the piemontite structure and unusual cation partitioning from natural piemontite–bearing parageneses suggest that oxygen fugacity during metamorphism may be a controlling factor in piemontite formation.

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Recent experimental work supports this suggestion (Anastasiou and Langer, 1976, 1977; Keskinen and Liou, 1979a,b). A combined field, petrographic, and chemical investigation was undertaken to clarify the metamorphic processes that permitted piemontite growth in the rocks near Shadow Lake in the eastern Sierra Nevada and to ascertain the correlation between experimental, theoretical, and natural evidence concerning piemontite stability.

SUMMARY OF REGIONAL GEOLOGY AND PETROGRAPHY[1]

The Shadow Lake piemontite zone is located within the Ritter Range roof pendant in the Devils Postpile Quadrangle, Calif. The roof pendant consists of a series of highly sheared metamorphosed volcanic and sedimentary units of Jurassic to possibly Permian age (Fiske and others, 1977; Tobisch and others, 1977) (fig. 1). The Shadow Lake piemontite zone was first recognized and described by Mayo (1932, 1933) and Short (1933). Mayo interpreted the dark pink schists as the result of Mn-enrichment due to the rise of "manganese–bearing emanations" along shear zones and fissures. Similar piemontite–bearing rocks have been noted in the Goddard Peak roof pendant (E. DuBray, personal commun.).

The metavolcanic rocks, which are cut at right angles to their strike by the Shadow Creek trail, consist of predominantly light to medium gray, coarse-to fine-grained crystal and lapilli tuffs, ash flows, and mafic flows, intercalated with siltstone and graywacke which may represent reworked pyroclastic material. Smooth, interfingering contacts between units and other sedimentary features suggest waterlain deposition. Bedding, schistosity, and shear features, as well as some of the veining and jointing, are roughly subparallel. The regional bedding and foliation trend N10°-35°W, with vertical to very high westward dips. The rocks show weak but pervasive foliation, with development of phyllitic to schistose textures in some units. The rocks are highly sheared, with tectonic shortening of up to 50 percent (Tobisch and others, 1977), and show abundant cataclastic features.

The piemontite zone consists of a 30 m thick hematite-rich sequence of lapilli and crystal tuff and chert sandwiched between two mafic, epidote-rich massive flows with intercalated tuff and graywacke. It is characterized by (1) sporadic occurrence of piemontite within fine-grained pink shaley and schistose layers, (2) by quartz + dark red piemontite veining, and (3) by the absence of the yellow-green epidote ubiquitous elsewhere in the pendant. The piemontite zone, as shown on the geologic map of the Devils Postpile Quadrangle by Huber and Rinehart (1965), is conspicuously long (6 km) and narrow (less than 30 m wide) and trends northwest-southeast.

The flows and tuffs stratigraphically above and below the piemontite zone are characterized by extensive development of epidote veins and lenticular pods aligned parallel to foliation. At the abrupt lower (eastern) contact, piemontite occurs as bright red prismatic crystals up

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[1] For details, see Keskinen (ms).

to 2 mm long in a matrix of quartz veins. The discontinuous veined quartz zone is about 30 cm wide and less than 50 m long. Uptrail from the contact with the lower epidote-bearing units, the crystal tuffs become more schistose, with the continued presence of piemontite reflected by the dark to light red color of the strata. Thin (2 to 5 cm) rosy pink, cherty layers, sheared and stretched volcanic lapilli, and spectacular irregular and podded segregations parallel the schistosity and add to the reddish striped appearance in outcrop. Upsection along Shadow Creek trail, a series of flakey light pink sericite schists, a purplish-red

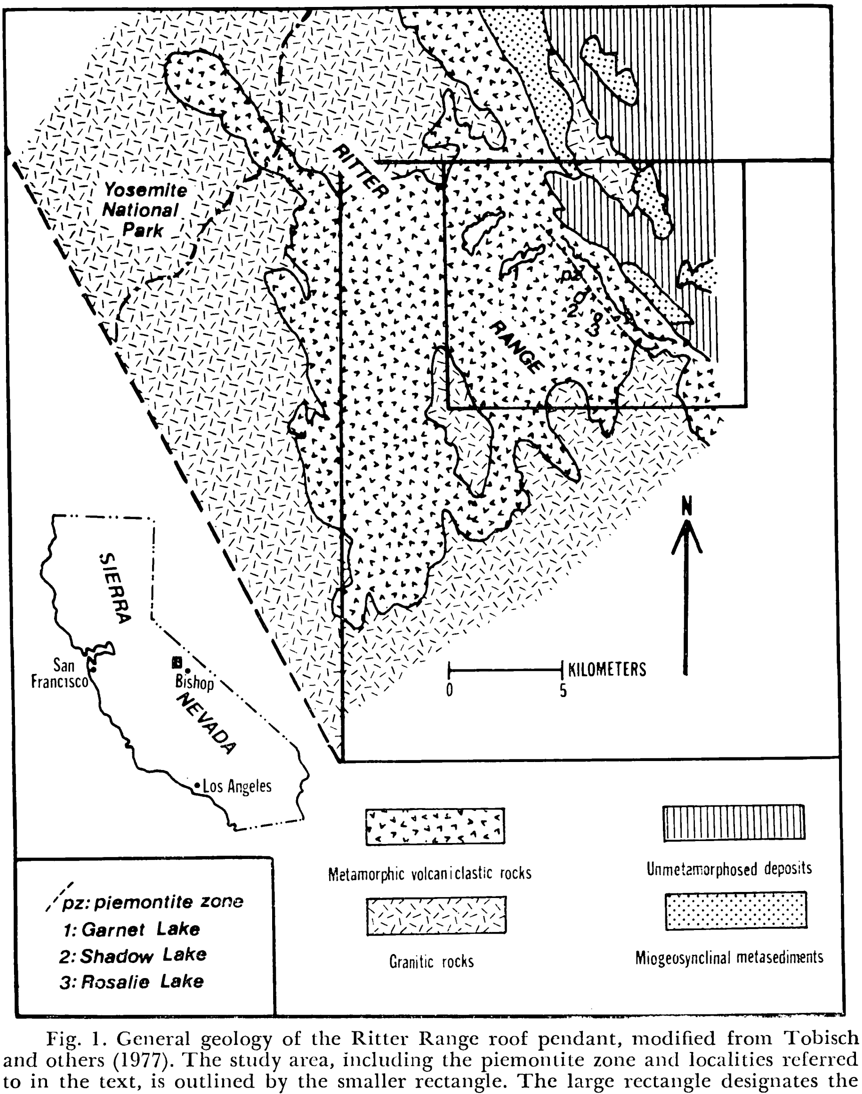

Fig. 1. General geology of the Ritter Range roof pendant, modified from Tobisch and others (1977). The study area, including the piemontite zone and localities referred to in the text, is outlined by the smaller rectangle. The large rectangle designates the Devils Postpile Quadrangle, also shown on the index map of California.

massive tuffaceous unit with a jasper-like appearance, fine-grained hematitic slatey tuff, and coarser-grained schistose crystal tuff with abundant chert bands and pods comprise the bulk of the piemontite zone.

Just north of Rosalie Lake (fig. 1), both the crystal and lithic tuffs of the piemontite zone and the epidote-rich schists occur. Quartz veining and piemontite + tremolite crystals and pods are more extensively developed than at the Shadow Lake locality. To the northwest, near Garnet Lake, the rocks stratigraphically equivalent to the Shadow Lake units show less distinct differentiation into piemontite and epidote units, but the lithologic sequence is similar to the Shadow Lake rocks.

In thin section, the rocks of the Shadow Lake units show clear evidence of their original pyroclastic nature and of a complex metamorphic/deformational history. Typical mineral assemblages from 17 samples are listed in table 1. In general, the textural relationships in the Shadow Lake rocks indicate several episodes of (or extended, continuous) crystallization of the metamorphic minerals, spanning, pre-, syn-, and post-tectonic metamorphism. The epidote-bearing units contain a fine-grained matrix of quartz + plagioclase + hematite + sericite, with varying proportions of blocky, subhedral plagioclase phenocrysts, epidote veins and pods, quartz phenocrysts, and amphibole crystals of varying habits. Other metamorphic minerals include muscovite, phlogopite, chlorite, sphene, and calcite. Despite considerable textural and compositional heterogeneity, the mineral assemblages of the quartz + piemontite veins and of the crystal and lithic tuffs of the piemontite zone are fairly similar: piemontite + quartz + feldspar + hematite + white mica + tremolite ± phlogopite ± chlorite ± garnet. Complex mutual replacement textures and foliation relations among the metamorphic minerals again suggest several periods of mineral growth. In both the epidote- and piemontite-bearing units, hematite is the dominant oxide and occurs as fine disseminated specks in the matrix and as blocky and skeletal porphyroblasts. Fine-grained hematite probably formed during devitrification. Large hematite grains occasionally show concentric zoning with included quartz and garnet bands, suggesting a metamorphic rather than a volcanic origin for large grains. In general, replacement textures, zoning, and other indications of disequilibrium are scarce, although not completely absent.

CHEMICAL ANALYSES OF WHOLE ROCK AND MINERAL COMPOSITIONS

Chemical compositions of various piemontite- and epidote-bearing rocks and of individual minerals were analyzed by electron microprobe. Analytical conditions and procedures were identical to those of Moore and Liou (1979).

Whole rock chemistry.—Analyses of ten representative rocks from a cross section of the lithologies at Shadow and Rosalie Lakes were obtained using the microprobe rock powder method (Moore and Liou, 1979), using similarly prepared rock standards. In addition, four samples from the piemontite-bearing lapilli tuffs and from the upper epidote-bearing zone were analyzed by Rapid Rock techniques at the U.S.

TABLE 1
Representative mineral parageneses from Shadow Lake metavolcanic rocks

Rock Type	Quartz & Piemontite Veins			Piemontite-Bearing Crystal Lithic Tuffs						Chert & Jasper-Like Units		Epidote-Bearing Units					
Sample No.	SL-4	RL-5	RL-6	SL-7	SL-24	GL-7	GL-4	RL-2	SL-26	SL-21	SL-40	SL-34	SL-60	GL-8	SL-63	SL-30	SL-66
Quartz	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Plagioclase	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Piemontite	X	X	X	X	*	X	X	X	tr	*	*						
Epidote												X	X	X	X	X	X
Garnet	X	X	X	X													
Tremolite	X	X			tr	X			X	X	X	X	X	X			X
Hematite	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Muscovite	X	X	X	X	X	X	X	X	X	X	X	X	X	tr	tr	X	X
Phlogopite	tr			tr	X		X	tr	X	X		X	tr			X	tr
Sphene															X		X
Chlorite							X			tr			X				
Calcite					X			X		X							
Rutile										X	X						

x = mineral is present in assemblage.
tr = trace amounts only.
* = pink-green intermediate piemontite.

Table 2

Whole rock chemical analyses (wt % oxides) and normative minerals of the Shadow Lake metavolcanics

ROCK TYPE	PIEMONTITE-RICH UNITS			EPIDOTE-BEARING UNITS					JASPER	PIEMONTITE CRYSTAL LITHIC TUFFS				
SAMPLE NO.	SL-7	RL-5	F73-1*	SL-63	SL-30	SL-34	SL-60	FT-71-70*	SL-40	SL-20	SL-26	SL-24	HT*	F71-51*
SiO_2	65.66	75.51	76.0	52.96	57.66	51.35	59.91	50.4	75.25	63.88	70.69	61.21	70.6	65.7
TiO_2	0.16	0.16	0.22	0.83	0.93	0.83	0.75	0.98	0.39	0.51	0.10	0.41	0.35	0.70
Al_2O_3	22.79	14.93	12.8	21.45	19.42	20.67	19.62	18.0	15.37	21.77	18.37	21.51	14.2	15.0
Fe_2O_3 **	2.01	1.91	1.9	5.56	9.23	8.49	6.01	6.1	3.21	4.05	1.19	3.46	2.6	4.8
FeO	--	--	0.6	--	--	--	--	4.2	--	--	--	--	1.1	0.2
MnO ***	0.55	0.49	0.33	0.34	0.10	0.18	0.15	0.18	0.03	0.04	0.11	0.05	0.06	0.14
MgO	2.23	2.54	1.7	1.28	3.18	5.66	1.51	4.4	0.59	1.45	0.96	1.46	1.5	1.8
CaO	1.07	4.55	2.1	12.09	2.16	9.18	5.92	6.9	0.99	2.52	2.90	4.61	1.3	3.9
Na_2O	0.73	1.96	1.7	2.43	0.82	2.35	3.01	3.4	0.95	2.99	2.06	3.09	2.1	3.2
K_2O	3.72	0.36	2.4	0.37	5.03	3.09	3.70	3.4	2.45	2.49	0.76	3.34	3.7	3.0
Anhydrous total	98.97	100.44	99.79	97.34	98.84	101.82	100.61	97.96	99.23	99.69	97.13	99.13	97.51	98.40
NORMATIVE MINERALS (VOLUME PROPORTIONS)														
K-FELDSPAR	21	2	12	2	30	18	22	19	14	14	4	18	23	18
ALBITE	6	16	13	23	7	7	27	21	8	26	17	26	20	29
ANORTHITE	5	21	9	48	11	37	29	23	5	12	14	21	7	17
CORUNDUM	15	3	8	-	9	-	-	-	9	10	9	9	5	-
DIOPSIDE	-	-	-	11	-	20	0.4	7	-	-	-	-	-	1
QUARTZ	45	50	50	10	21	-	10	-	58	30	52	17	37	24
ENSTATITE	8	8	7	6	21	-	11	-	6	9	4	8	9	10
OLIVINE	-	-	-	-	-	10	-	27	-	-	-	-	-	-
NEPHELINE	-	-	-	-	-	7	-	4	-	-	-	-	-	-
Mn_2O_3/Fe_2O_3	0.30	0.28	0.19	0.068	0.012	0.024	0.028	0.02	0.008	0.010	0.097	0.017	0.02	0.03

* Rapid rock chemical analyses, U.S.G.S.

** Total Fe expressed as Fe_2O_3.

*** Total Mn expressed as MnO.

Geological Survey and generously donated by Drs. Ronald Kistler and Richard Fiske. These chemical analyses, along with their normative minerals, are listed in table 2. Normative calculations may not be entirely appropriate for all the units, as some rocks may contain a significant detrital component incorporated during sedimentary recycling of pyroclastic material. However, normative compositions are useful for comparisons among the epidote- and piemontite-bearing rocks. As shown in figure 2, based on Streckeisen's 1967 diagram for volcanic rocks, the compositional ranges for these units are extensive. In general, the lapilli and crystal tuffs of the piemontite zone fall within the compositional ranges of rhyodacite and dacite. The more mafic nature of the epidote-bearing strata is shown by the clustering of their compositions in the fields of latite andesite, latite basalt, and tholeiitic basalt.

The *Handbook of Geochemistry* (Wedepohl, 1969) lists average MnO contents of various igneous rock types ranging from 0.05 wt per-

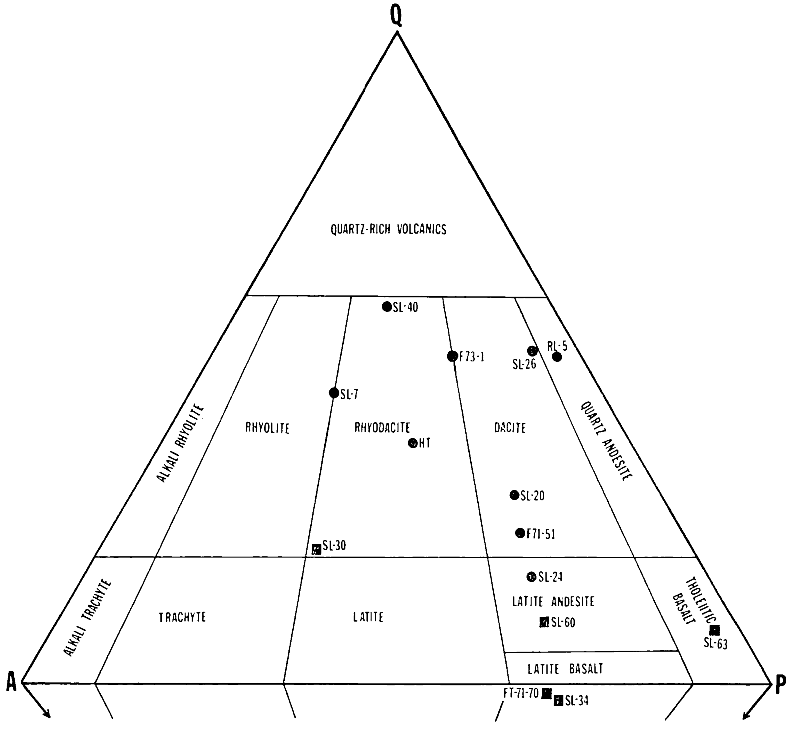

Fig. 2. Normative mineralogies of the Shadow Lake metavolcanic units. Diagram is based on Streckeisen's 1967 classification of volcanic rock types. Square symbols indicate epidote-bearing units; filled circles indicate piemontite-bearing units.

A = alkali feldspar; Q = quartz; P = plagioclase feldspar; F = feldspathoids.

TABLE 3

Chemical analyses of epidote minerals and garnets from Shadow Lake metavolcanics (wt percent oxides)

SAMPLE NO.	YELLOW-PINK PIEMONTITE			VEIN PIEMONTITE		PINK-GREEN PIEMONTITE		YELLOW-GREEN EPIDOTES			PIEMONTITE		GARNETS			
	GL-7	GL-4	RL-2	RL-6	SL-4	SL-40	SL-21	SL-60	GL-8	SL-34	SHORT,1933		RL-6-1	RL-6-2	SL-4-A	SL-4-B
SiO_2	37.38	38.10	38.29	38.31	37.57	37.58	38.05	37.97	37.59	37.52	35.26	SiO_2	37.87	37.95	37.45	37.39
Al_2O_3	23.83	23.89	21.95	25.99	22.15	22.54	23.53	20.90	22.66	21.37	23.50	Al_2O_3	20.19	20.23	17.63	17.53
Fe_2O_3	11.08	12.97	12.90	6.72	8.19	13.36	12.49	16.01	14.91	15.35	4.65	Fe_2O_3*	1.63	1.59	1.60	1.79
Mn_2O_3	3.22	2.52	2.96	3.96	7.53	2.25	1.17	0.38	0.54	0.31	12.13	MnO***	35.57	35.49	36.41	31.87
MgO	0.09	0.20	0.09	0.20	0.08	0.08	0.05	0.05	0.13	0.16	0.21	MgO	1.73	1.72	0.56	0.62
CaO	22.38	21.91	21.89	27.27	23.14	22.10	23.19	23.03	22.47	23.72	22.73	CaO	3.98	4.12	4.68	9.12
Na_2O	0.00	0.00	0.01	0.03	--	0.04	0.01	0.03	0.11	0.04	--	Na_2O	--	--	--	--
K_2O	0.05	0.03	0.04	--	--	0.05	0.04	0.05	0.15	--	--	K_2O	0.06	0.07	--	--
Anhydrous total	98.04	99.63	98.13	98.48	98.66	98.00	98.54	98.44	98.57	98.46	99.97		101.03	101.18	98.32	98.32
ATOMIC PROPORTIONS, O = 25												O = 12				
Si	6.04	6.00	6.10	5.99	5.98	6.00	6.02	6.08	5.98	6.01		Si	3.04	3.04	3.12	3.10
Al(IV)	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.02	--		Al(IV)	--	--	--	--
Al(VI)	4.26	4.44	4.12	4.78	4.14	4.24	4.39	3.94	4.23	4.03		Al(VI)	1.91	1.91	1.73	1.71
Fe(+3)	1.34	1.54	1.55	0.79	0.98	1.61	1.49	1.93	1.78	1.85		Fe(+3)	0.10	0.10	0.10	0.11
Mn(+3)	0.40	0.30	0.36	0.47	0.91	0.27	0.14	0.05	0.07	0.04		Mn(+2)	2.42	2.41	2.57	2.24
Mg	0.02	0.05	0.02	0.05	0.02	0.02	0.01	0.01	0.03	0.04		Mg	0.21	0.21	0.07	0.08
Ca	3.88	3.53	3.74	3.90	3.95	3.78	3.93	3.95	3.83	4.07		Ca	0.34	0.35	0.42	0.81
K	0.01	0.01	0.01	0.01	--	0.01	0.00	0.01	0.03	0.01		K	0.01	0.01	--	--
Na	0.00	0.00	0.00	--	--	0.01	0.01	0.01	0.03	--		Na	--	--	--	--
MOLECULAR PERCENT END MEMBER COMPONENTS																
CLINOZOISITE	71.0	70.7	68.4	79.1	68.6	69.3	73.0	66.6	69.6	68.1		ANDRADITE	3.3	3.2	3.3	3.5
PISTACITE	22.3	24.5	25.6	13.1	16.3	26.2	24.7	32.6	29.3	31.3		GROSSULAR	8.4	8.9	10.4	22.4
PIEMONTITE	6.6	4.8	6.0	7.8	15.1	4.5	2.3	0.8	1.1	0.6		SPESSARTINE	80.5	81.0	84.0	71.7
												PYROPE	6.9	6.9	2.3	2.5

* Total Fe expressed as Fe_2O_3.

** Total Mn expressed as Mn_2O_3.

*** Total Mn given as MnO.

cent for granites to 0.11 wt percent for dacites to 0.18 wt percent for basalts. Most sedimentary rocks (an exception being manganiferous cherts) similarly show low MnO values on the order of 0.03 wt percent for sandstones to 0.16 wt percent for pelitic rocks. All but four of the analyzed Shadow Lake rocks fall within this range and have nearly constant MnO contents of 0.03 to 0.20 wt percent. SL-7, RL-5, SL-63, and F73-1, however, are comparatively rich in MnO (0.33 to 0.55 wt percent). Not coincidentally, three of these rocks are from near or within quartz + piemontite veins. One Mn-rich rock is an epidote-bearing unit. Fe_2O_3 is generally higher for the epidote-bearing units than for the tuff units; Fe^{+3} is very low in the most Mn-rich piemontite-bearing units, reflected in anomalously high Mn/Fe ratios. Whether piemontite or epidote occurs within a given rock does not appear to be related to these compositional characteristics.

The valence state in which Fe and Mn are present in a mineral cannot be determined routinely using the electron microprobe. Based on mineralogical arguments, total iron was calculated as Fe_2O_3 for epidote minerals, garnets, muscovites, and rocks and as FeO in phlogopites, chlorites, and amphiboles. Manganese was considered trivalent in epidote minerals and muscovite, divalent in all other minerals and in the whole rock analyses. Although both divalent and trivalent forms of both elements are undoubtedly present in these individual minerals, examination of structural formulas for the various minerals in general substantiated these choices. The high Fe_2O_3/FeO ratios for the four U.S. Geological Survey analyses show that these rocks are indeed highly oxidized. The mafic rock FT-71-70, with Fe_2O_3/FeO ratio of 1.5, is already ferric iron-rich, whereas rocks from the Mn zone and tuffaceous units have an even higher range from 2.4 to 30. Discussion of the significance of this oxidized state will be deferred to a later section.

Epidote minerals.—Microprobe analyses of epidotes and piemontites from 10 samples, along with calculated structural formulas and end-member compositions, are listed in table 3. A wet chemical analysis of piemontite from this area by Short (1933) is included for comparison. No appreciable compositional variation was detected within grains.

Epidote in the more mafic layers is light yellow and mildly pleochroic in thin section, sometimes showing a slight pink tinge. In the quartz + piemontite veining at the lower contact of the zone, piemontite is brightly pleochroic (crimson-violet-yellowish orange). Away from the contact zone, piemontite shows considerable variability, from lighter shades of pink and yellow in the crystal tuffs to "watermelon" pink to greenish intermediate pleochroism in the cherty and jasper-like units.

Cell parameters for five piemontites and two epidotes from the Shadow Lake area were determined using quartz as an internal standard and the least squares cell parameter refinement program of Appleman, Evans, and Hardwerker (1972). The results are listed in table 4. Piemontite cell parameters are quite uniform, with average values of $a =$ 8.87(1)Å, $b =$ 5.66(1)Å, $c =$ 10.17(2)Å, and $\beta =$ 115° 22′ for the five samples. Yellow-green epidotes have a slightly larger unit cell, with $a = 8.90(1)$Å, $b = 5.649(9)$Å, $c = 10.18(2)$Å, and $\beta = 115° 22'$.

Compositions of the analyzed epidotes and piemontites are plotted in a ternary diagram in figure 3. There are, in terms of octahedral (Fe^{+3}–Mn^{+3}–Al) occupancy, four groups corresponding to yellow-green epidotes, intermediate pink-green piemontites, piemontites from the main body of the piemontite zone, and vein piemontites from near the lower contact. The correlation between pleochroic color of the epidote minerals and composition is not surprising; the red and green colorations of piemontite and epidote (pistacite), respectively, have always been attributed to Mn^{+3} and Fe^{+3} in the octahedral sites (Burns, 1970). The epidotes from the mafic rocks have relatively uniform compositions, falling within the range $\mathrm{Ps}_{24\text{-}33}\mathrm{Pm}_{0.6\text{-}1.4}\mathrm{Cz}_{65\text{-}73}$, despite a variation of color in hand specimen from golden yellow to pistachio green. Other substitutions such as Al for Si or Mg, Na, Fe^{+2} for Ca are relatively minor. The presence of Mn^{+2} substituting for Ca in common epidotes has been suggested as responsible for the non-development of the pinkish piemontite pleochroic scheme (for example, Smith and Albee, 1967). Structural formula calculations suggest that Mn in the analyzed epidotes is trivalent and substitutes for Fe + Al; the green color of the epidotes is a result of the great predominance of Fe over Mn in the octahedral sites. Indeed, the pinkish tinge of some of the epidotes in thin section may be a clue to the presence of small amounts of Mn^{+3}.

Both detailed single crystal refinements (Dollase, 1969) and evidence from Mössbauer and polarized absorption spectra (Burns and Strens, 1967; Bancroft, Maddock, and Burns, 1969; Dollase, 1973) have suggested that Fe and Mn tend to be concentrated within one of the three octahedral sites, the "between-chain" M(3) site, in the epidote structure. This preferred substitution is theoretically supported by both ionic size criteria and by a gain of crystal field stabilization energy due to the presence of Mn^{+3} in the highly distorted site. The idea that epidotes with substitution of (Fe + Mn) for Al near the maximum "limit" of

TABLE 4

Cell parameters from natural piemontites and epidotes from the Shadow Lake metavolcanics

SAMPLE NUMBER	a (Å)	b (Å)	c (Å)	β	V (Å³)	
RL-4	8.88(2)	5.631(7)	10.19(2)	115°24'	459.3(8)	
SL-55	8.87(1)	5.651(7)	10.16(1)	115°23'	459.2(7)	PIEMONTITES
SL-4	8.87(2)	5.649(9)	10.18(2)	115°18'	460(1)	
Mn Zone	8.87(1)	5.650(6)	10.18(1)	115°16'	460.4(6)	
GL-7	8.86(3)	5.72(3)	10.13(3)	115°14'	464(2)	
SL-31	8.91(1)	5.642(6)	10.20(2)	115°17'	463.0(7)	EPIDOTES
SL-60	8.88(1)	5.657(8)	10.15(2)	115°28'	466(1)	

33 percent may be related to low-temperature crystallization, with an expansion of the range of epidote compositions as metamorphic grade increases, is a prevalent one, following Miyashiro and Seki's 1958 study. Coombs, Nakamura, and Vuagnat (1976) suggested that this spread of compositional range toward clinozoisite with rising temperature may rather be attributable to a "general tendency for decreasing f_{O_2} or the availability of additional $Ca_2Al_3Si_3O_{12}(OH)$ component with advancing metamorphism." In the Shadow Lake units, the observed high degree of Fe + Mn substitution may be a result of the predominance of Fe^{+3} over Fe^{+2} in these very oxidized rocks.

Garnets.—Garnets from two samples were analyzed, and the results, together with their structural formulas and endmember compositions, are listed in table 3. Although quite variable in composition, within individual grains these garnets show little systematic zonation. In a few grains, slight enrichment of Mn in the cores with respect to the rims was detected. Garnets in the piemontite border zone are colorless, elongate, and strained, as evidenced by fracturing, bending, and considerable birefringence. A few later euhedral garnets crosscut the schistosity. No significant difference in composition between the two genera-

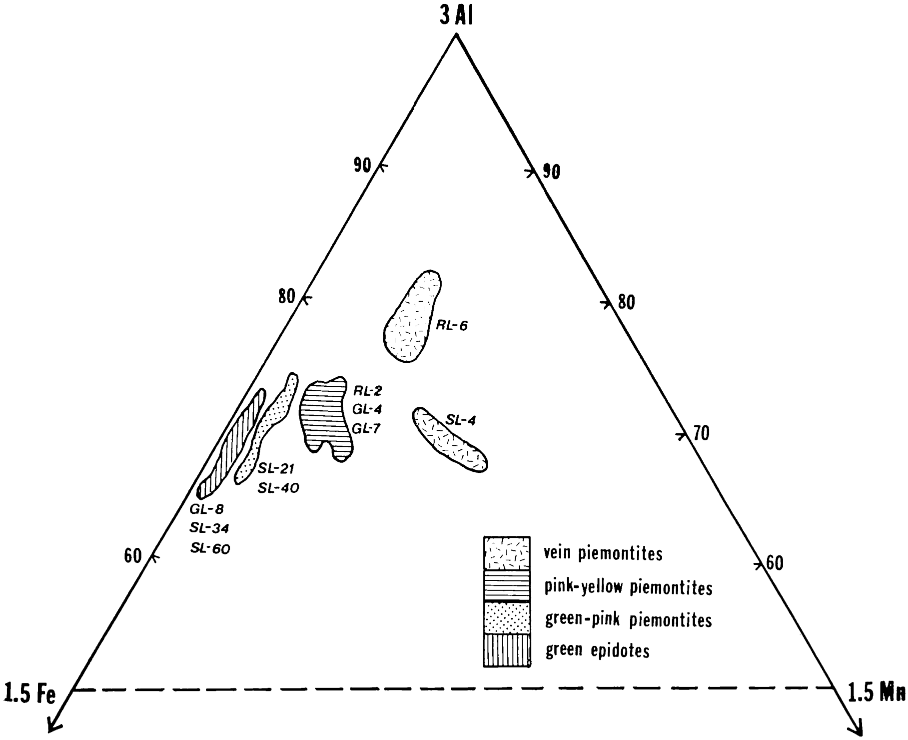

Fig. 3. Compositional ranges of analyzed piemontites and epidotes from the Shadow Lake area, based on occupancy of the three octahedral M sites. Sample numbers included within a field are shown.

tions and habits of garnet was found. All garnets are spessartine-rich, with the range of composition $Sp_{77\text{-}84}Gr_{8\text{-}22}And_{3.1\text{-}3.5}Py_{2\text{-}7}$. Structural formula calculations suggest that most or all the Fe in the analyzed garnets must be present as ferric andradite component.

Muscovite.—Six muscovite analyses from three samples listed in table 5 show fairly high Fe + Mg contents, qualifying marginally as phengites, but only moderate Mn_2O_3. Total Mn and Fe are expressed as Fe_2O_3 and Mn_2O_3 because crystallographic, Mössbauer, and optical absorption analyses have indicated that Mn^{+3} and Fe^{+3} are the dominant octahedral species in pinkish muscovites (Annersten and Hålenius, 1976). In outcrop, the muscovites in the piemontite-bearing schists show a distinct pinkish tinge; in thin section they are colorless. Pink muscovites described in the literature are generally somewhat higher in Mn_2O_3 (0.34-0.65 wt percent) than the Shadow Lake micas. As suggested by Gresens and Stensrud (1977), it appears to be "oxidation state of the manganese, rather than absolute concentration, that accounts for the red tint." Paragonite content is low in the analyzed muscovites. Fe/Fe+Mg ratios range from 0.1 to 0.8. The analyzed samples contain moderate amounts of Fe^{+3}, and the very low Mn/Fe ratios suggest a scarcity of Mn^{+3} relative to Fe^{+3}. The muscovites from the cherty unit (SL-21) have both low Fe and Mn, suggesting low contents of these elements in the rock. The piemontite-bearing unit (RL-2) contains muscovite with somewhat higher Mn^{+3} than that from the other rocks.

Phlogopites.—Occurrences of Mg-rich phlogopites are often described from metamorphosed marbles and ultramafic rocks, but phlogopites from schists of pelitic or silicic to intermediate volcanic compositions are rare. Such parageneses have been documented from localities where special conditions (high oxygen fugacity, low hydrogen fugacity) prevailed during metamorphism (Smith and Albee, 1967; Stensrud and Gresens, 1973). Microprobe analyses of the pale yellow phlogopites from this study are listed in table 5. Phlogopites from epidote-bearing rocks have lower average Mn/Fe and higher average Fe/Fe+Mg ratios (0.10 and 0.24, respectively) than those from piemontite-bearing rocks (0.63 and 0.11), largely due to higher FeO contents of the mafic rocks. MnO is considerably higher in phlogopites from piemontite rocks, due perhaps partly to the effects of whole rock chemistry. Both Fe and Mn are considered dominantly divalent in phlogopite solid solution (Deer, Howie, and Zussman, 1962). The uniformly low values for both elements suggest oxidizing conditions that would favor incorporation of Mg in preference to divalent transition metals. Comparison with the compositions of muscovites further supports this suggestion. The significantly higher Fe/Fe+Mg and slightly lower Mn/Fe in muscovites than in phlogopites from corresponding rocks suggest that f_{O_2} conditions were high enough to stabilize most of the available Fe in the ferric state but not sufficiently high as to cause Mn^{+3} to be the dominant ionic species. The available Mn^{+3} may have been partitioned into the epidote minerals due to crystal-chemical controls. TiO_2 was measured in phlogopites from RL-2 and ranges in value from 0.99 to 1.48 wt percent.

TABLE 5

Chemical analyses of micaceous minerals from the Shadow Lake metavolcanics (wt percent oxides)

	MUSCOVITES						PHLOGOPITES					
	EPIDOTE UNITS		CHERT		PIEMONTITE TUFFS		EPIDOTE UNITS			JASPER	PIEMONTITE UNITS	
	SL-60-4	SL-60-5	SL-21-2	SL-21-3	RL-2-2	RL-2-5	SL-34-5	SL-34-6	GL-8	SL-40	GL-4	RL-6
SiO_2	47.94	46.62	47.43	45.57	44.71	44.67	39.96	40.71	41.77	40.61	40.97	41.07
Al_2O_3	30.00	28.25	33.15	37.09	32.31	35.44	16.14	16.22	18.31	16.18	18.32	16.04
Fe_2O_3*	4.05	5.30	0.37	0.18	3.82	3.39	--	--	--	--	--	--
FeO*	--	--	--	--	--	--	6.15	6.24	3.09	2.11	2.22	1.95
Mn_2O_3**	0.04	0.04	0.07	0.05	0.44	0.11	--	--	--	--	--	--
MnO*	--	--	--	--	--	--	0.42	0.44	0.49	1.03	0.85	2.04
MgO	1.95	1.96	1.51	0.55	2.07	0.42	20.66	20.87	21.87	22.12	22.78	23.51
CaO	0.01	0.00	0.32	0.22	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.00
K_2O	10.00	9.47	11.04	11.00	9.34	9.24	11.09	9.36	10.11	9.28	9.25	9.36
Na_2O	0.24	0.65	0.21	0.23	0.31	0.35	0.07	0.07	0.10	0.02	0.06	0.09
Anhydrous Total	94.24	92.29	94.14	94.88	92.55	93.27	95.17	94.61	95.78	91.80	95.45	94.27
					ATOMIC PROPORTIONS, O = 22							
Si	6.45	6.46	6.37	6.07	6.12	6.03	5.79	5.86	5.90	5.90	5.81	5.83
Al(IV)	1.53	1.54	1.63	1.93	1.88	1.96	2.21	2.14	2.10	2.10	2.19	2.17
Al(VI)	3.24	3.07	3.62	3.89	3.33	3.68	0.54	0.61	0.95	0.67	0.80	0.51
Fe (+3)	0.41	0.55	0.04	0.02	0.39	0.34	--	--	--	--	--	--
Fe (+2)	--	--	--	--	--	--	0.75	0.75	0.37	0.26	0.26	0.23
Mn (+3)	0.00	0.00	0.01	0.01	0.05	0.01	--	--	--	--	--	--
Mn (+2)	--	--	--	--	--	--	0.05	0.05	0.06	0.13	0.10	0.25
Mg	0.39	0.40	0.03	0.11	0.42	0.08	4.46	4.48	4.26	4.79	4.70	4.97
Ca	0.00	0.00	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
K	1.72	1.67	1.89	1.87	1.63	1.59	2.05	1.72	1.82	1.72	1.63	1.69
Na	0.06	0.17	0.05	0.06	0.08	0.09	0.02	0.02	0.03	0.01	0.02	0.02
Fe/Fe + Mg	0.5	0.6	0.1	0.2	0.5	0.8	0.14	0.14	0.07	0.05	0.05	0.04
Mn/Fe	0.0	0.0	0.25	0.5	0.1	0.03	0.07	0.07	0.16	0.50	0.38	1.09

* Total Fe expressed as Fe_2O_3 or FeO. ** Total Mn expressed as Mn_2O_3 or MnO.

TABLE 6
Chemical analyses of tremolites and chlorites from the Shadow Lake metavolcanics (wt percent oxides)

	TREMOLITES									CHLORITES		
ROCK TYPE	PIEMONTITE & QUARTZ VEINS		CRYSTAL TUFFS		CHERT		EPIDOTE-BEARING UNITS			LAPILLI TUFF		
SAMPLE NO.	SL-4	RL-6	GL-7-7	GL-7-A	SL-21-4	SL-21-3	SL-34	SL-60	GL-8	GL-4-1	GL-4-2	GL-4-4
SiO_2	55.38	58.04	54.15	54.40	57.33	56.44	55.13	56.72	53.61	32.09	32.18	34.88
Al_2O_3	1.65	2.66	2.91	2.32	1.29	2.86	3.42	2.63	4.42	21.18	21.72	19.89
FeO*	0.75	0.77	2.18	0.97	0.72	1.33	3.93	3.15	2.92	0.68	0.44	0.31
MnO**	0.25	2.63	2.33	2.38	1.24	2.95	--	1.35	1.17	1.07	0.88	0.87
MgO	26.28	20.81	19.87	21.17	22.35	21.13	21.15	21.22	20.54	31.63	31.99	30.21
CaO	13.30	12.55	12.52	12.77	13.32	12.32	13.36	12.83	12.81	0.00	0.00	0.01
Na_2O	--	0.17	0.36	0.26	0.11	0.24	0.38	0.40	0.59	0.00	0.00	0.00
K_2O	--	--	0.09	0.07	0.05	0.08	0.35	0.20	0.26	0.03	0.08	0.06
Anhydrous total	97.70	98.17	95.05	94.86	96.71	98.00	98.14	99.07	96.32	86.67	87.31	86.30
	ATOMIC PROPORTIONS, 0 = 23									ATOMIC PROPORTIONS, 0 = 28		
Si	7.58	7.93	7.75	7.76	7.93	7.80	7.64	7.78	7.54	5.98	5.94	6.47
Al(IV)	0.27	0.07	0.25	0.24	0.07	0.20	0.36	0.22	0.46	2.02	2.06	1.53
Al(VI)	0.00	0.36	0.24	0.15	0.14	0.26	0.20	0.20	0.27	2.63	2.67	2.82
Fe(+2)	0.09	0.09	0.26	0.12	0.08	0.15	0.46	0.36	0.34	0.11	0.07	0.05
Mn(+2)	0.03	0.31	0.28	0.29	0.15	0.35	--	0.16	0.14	0.17	0.14	0.14
Mg	5.36	4.24	4.24	4.50	4.61	4.35	4.37	4.34	4.31	8.78	8.81	8.35
Ca	1.95	1.84	1.92	1.95	1.97	1.82	1.98	1.88	1.93	--	--	--
Na	--	0.05	0.10	0.07	0.03	0.06	0.10	0.10	0.16	0.00	0.00	0.00
K	--	--	0.02	0.01	0.01	0.01	0.06	0.04	0.05	0.01	0.02	0.01
	MOLECULAR PERCENT END MEMBERS											
TREMOLITE	98.0	85.0	84.0	89.0	93.0	85.0	87.0	86.0	85.0	--	--	--
ACTINOLITE	1.5	1.8	5.0	2.3	1.7	3.0	9.0	7.0	7.0	--	--	--
PARGASITE	--	7.2	4.8	3.0	3.0	5.0	4.0	4.0	5.4	--	--	--
"Mn"	0.5	6.1	5.6	5.7	3.0	6.0	-	3.0	8.7	--	--	--

* Total Fe expressed as FeO.

** Total Mn expressed as MnO.

Chlorites.—Interpretation of chlorite composition in terms of the conditions of metamorphism is less straightforward. Colorless to light green chlorite crystals were analyzed from a sample of piemontite-bearing lapilli tuff (table 6). Both field evidence and thin-section textures suggest that the chlorites are late stage replacements of micas and other earlier metamorphic phases. X-ray diffraction patterns indicate that these are 14Å chlorites. Using Hey's chlorite classification scheme (1954), these chlorites, with Fe/Fe+Mg = 0.012, Si = 5.9 to 6.5, and Mn/Fe = 1.59 to 2.85, are designated as clinochlore and penninite. MgO is very high, MnO and FeO rather low. The Fe/Fe+Mg ratio of chlorites from pelitic rocks usually lies within the range of 0.2 to 0.8 (Miyashiro, 1973). In moderately low-grade metamorphic rocks, the lower Fe/Fe+Mg ratio for the analyzed chlorites may be attributed to (1) continuing highly oxidizing conditions with most Fe present as ferric iron or (2) a relict relationship between the composition of the chlorite and that of the mineral which it is replacing, in this case, Mg-rich micas.

Tremolite.—Fibrous colorless to very pale yellow tremolite occurs in almost all the epidote- and piemontite-bearing schists. Nine microprobe analyses of tremolites are listed with their calculated structural formulas and endmember components in table 6. The analyzed tremolites are Fe-poor and range from $Tr_{84\text{-}98}$; these compositions are certainly not characteristic of greenschist facies amphiboles from intermediate metaigneous rocks. The Mg-rich compositions, like those of the phlogopites, must be because of high f_{O_2} prevailing during metamorphism and consequent unavailability of Fe^{+2}. MnO is variable in the tremolites, ranging from 0.02 to 2.95 wt percent. Other substitutions (Na for Ca, octahedral Al) are relatively minor. Approx 0.6 wt percent TiO_2 was detected in tremolites from sample GL-8.

The tremolite compositional data are consistent with an interpretation of a high f_{O_2} condition, intermediate between the upper limits of Fe_3O_4 and Mn_3O_4 stability such that the available Fe would all be ferric, but Mn would only be partially oxidized to Mn^{+3}. Hence Fe, usually ferrous in the octahedral sites of amphibole, would be largely excluded, and Mn (as Mn^{+2}) would merely reflect the bulk Mn content of the rock and the degree of competition by other phases. Mn/Fe is greater than 1 for tremolites coexisting with piemontite, and Mn/Fe is less than 1 for tremolites coexisting with green epidote. Higher Fe contents in tremolites associated with epidote may indicate slightly lower f_{O_2} and more Fe^{+2} available during crystallization, perhaps due to coupled breakdown of hematite which resulted in the release of Fe. Alone, however, this evidence is permissive rather than conclusive, and the influence of bulk composition is difficult to isolate.

Feldspars.—Plagioclase compositions reflect the variable and disequilibrium state of the feldspars in these rocks. Optical determination indicates albite compositions; microprobe analyses range from albite to andesine ($Ab_{69\text{-}93}An_{2\text{-}34}Or_{1\text{-}8.5}$). Textural evidence and the metamorphic association favor the interpretation that this compositional heterogeneity is the result of incomplete albitization of the relict phenocrysts, which were undoubtedly more calcic initially in some of the units.

Opaque phases.—Microprobe analyses for three hematite porphyroblasts show an average of 98 wt percent Fe_2O_3 with minor amounts (0.42 and 0.36 wt percent) of Mn_2O_3 and Al_2O_3. TiO_2 was determined for one sample to be 3.6 wt percent. The moderate TiO_2 content helps account for the sphene reaction rims prevalent around large hematites in the epidote-bearing rocks, which suggest a breakdown relation of titanhematite to hematite and sphene under the influence of Ca-bearing fluids. Intergrowth of calcite + hematite in the veins of sample GL-77B may also reflect late stage metamorphic reactions involving Fe-Ca enriched fluids, with f_{O_2} remaining sufficiently high that hematite was still stable.

Calcite.—Calcite is obviously a late-stage metamorphic hydrothermal mineral in these rocks. Calcite veins crosscut all foliations and are involved in replacement of amphiboles, micas, feldspars, and hematite. Analyses of three calcite grains indicate that the carbonate is fairly pure $CaCO_3$ (98 wt percent), with moderate MnO (0.09-2.47 wt percent) and minor amounts of Fe and Mg.

INTERCRYSTALLINE CATION PARTITIONING: A DISCUSSION

Table 7 presents compositions of coexisting minerals from the various rock types near Shadow Lake. Examination of the cation ratios of individual minerals yields several conclusions regarding metamorphism of these rocks. Bulk compositions, especially Fe, Mn, and Mg, may have had a significant effect on mineral chemistries. Cherty and jasper-like units, low in MnO, contain piemontite with low Mn contents even though f_{O_2} conditions may have favored inclusion of larger amounts of Mn^{+3}. The Fe-rich nature of the basaltic units may have caused tremolite and phlogopite to be correspondingly higher in iron content (and hence with slightly lower Mn/Fe) than for other units.

Under extremely oxidizing conditions of metamorphism, normally ferrous-iron-bearing solid solutions would tend to be enriched in the Mg endmember. We can differentiate more finely from partitioning of Fe, Mg, and Mn among coexisting phases as to what degree of oxidation may have prevailed during metamorphism. Several lines of evidence suggest that the oxidation state of these rocks was borderline between the stability regimes of Fe^{+3} and Mn^{+3}. Mn requires higher f_{O_2} in order to be fully oxidized to a trivalent state than does Fe. Piemontites and epidotes both have high Fe^{+3}, reflecting in part the availability of ferric iron and the lack of other phases (except hematite) capable of incorporating large amounts of Fe^{+3}. Mn^{+3} in yellow epidotes is low, however; the higher Mn in piemontites suggests that more Mn^{+3} was available (higher f_{O_2}). Low Mn^{+2} contents of tremolites and high Mn^{+3} contents of the piemontites from the contact zone (SL-4) suggest locally higher f_{O_2} (and hence higher Mn^{+3}/Mn^{+2}), possibly controlled by fluids in an "open-system" situation. All predominantly divalent transition metal-bearing minerals are very low in Fe but moderately high in

TABLE 7

Chemical compositions of coexisting mineral assemblages from the Shadow Lake metavolcanics

	SL-34, LOWER EPIDOTE ZONE			GL-4, PM CRYSTAL TUFFS			GL-8, GARNET LAKE EPIDOTE ZONE		
	EPIDOTE	TREMOLITE	PHLOGOPITE	PIEMONTITE	CHLORITE	PHLOGOPITE	EPIDOTE	TREMOLITE	PHLOGOPITE
SiO_2	37.52	55.13	40.71	37.77	34.88	40.97	37.59	53.61	41.77
Al_2O_3	21.37	3.42	16.22	24.19	19.89	18.32	22.66	4.42	18.31
Fe_2O_3	15.35	--	--	12.46	--	--	14.91	--	--
FeO	--	3.93	6.24	--	0.31	2.22	--	2.92	3.09
Mn_2O_3	0.31	--	--	3.39	--	--	0.54	--	--
MnO	--	--	0.44	--	0.87	0.85	--	1.17	0.49
MgO	0.16	21.15	20.87	0.19	30.21	22.78	0.13	20.54	21.87
CaO	23.72	13.36	--	21.48	0.00	0.00	22.47	12.81	0.03
K_2O	0.04	0.35	9.36	0.04	0.06	9.25	0.15	0.26	10.11

	RL-6, QUARTZ + PM VEINING				SL-60, UPPER EPIDOTE ZONE			SL-21, CHERTY POD, UPPER PM ZONE		
	PIEM.	GARNT.	TREM.	PHLOGOP.	EPIDOTE	TREMOLITE	MUSCOVITE	PIEMONTITE	MUSCOVITE	TREMOLITE
SiO_2	38.58	37.59	50.08	41.07	37.97	56.72	47.94	37.97	45.57	57.33
Al_2O_3	25.20	20.23	2.66	16.04	20.90	2.63	30.00	23.29	37.09	1.29
Fe_2O_3	7.80	1.59	--	--	16.01	--	4.05	13.40	0.18	--
FeO	--	--	0.77	1.95	--	3.15	--	--	--	0.72
Mn_2O_3	4.60	--	--	--	0.38	--	0.04	1.39	0.05	--
MnO	--	35.49	2.63	2.04	--	1.35	--	--	--	1.24
MgO	0.09	1.72	20.81	23.51	0.05	21.22	1.95	0.07	0.55	22.35
CaO	22.33	4.12	12.55	--	23.03	12.83	0.01	22.91	0.22	13.32
K_2O	0.04	0.07	--	9.36	0.05	0.40	10.00	0.04	11.00	0.05

Mn, suggesting further that during crystallization of these phases, Fe was predominantly ferric, but Mn may still have been mostly divalent. Slightly higher Fe contents in tremolites from epidote units may indicate slight amounts of Fe^{+2} (lower f_{O_2}) available during their growth. Comparison of chlorite and phlogopite in GL-4 or of tremolite and phlogopite from RL-6 (table 7) show approximately similar MnO contents but higher Fe in the phlogopites, possibly due to the ability of this mineral to accommodate small amounts of Fe_2O_3 (Deer, Howie, and Zussman, 1962). Muscovite has low Mn/Fe; if trivalent ions were favored in its structure as replacement for Al in the octahedral sites, this would again be in accordance with a Fe^{+3}-rich, Mn^{+3}-deficient fluid condition. Mn shows a strong preference for partitioning into garnets in low-grade metamorphic rocks. (See discussions by Miyashiro, 1953, 1973; Atherton, 1965). The presence of Mn^{+2} and presumably Fe^{+3} in the garnets from two samples (RL-6 and SL-4) support the estimation of oxygen fugacity.

Thus, it appears that in the epidote units, f_{O_2} conditions were such that Fe^{+3} and Mn^{+2} were the dominant ionic species for these transition elements. In the piemontite-bearing units, Fe^{+3}, Mn^{+2}, and Mn^{+3} were all available during metamorphism, indicative of a slightly higher f_{O_2}, above the hematite–magnetite transition yet below the Mn_2O_3 field of stability. It should also be considered that in the epidote-bearing rocks, not only was Fe_2O_3 content higher, but it may have been more readily available and mobile in the fluid. Reaction of titanhematite with Ca-bearing solutions to form sphene may have released Fe, triggering compositional readjustments. However, much of the iron in the piemontite units may have been tied up in stable, fine-grained hematite early in the metamorphic process, making the "effective" Fe content of the rocks much lower.

METAMORPHIC HISTORY OF THE SHADOW LAKE UNITS

Origin of the piemontite.—Textural, field, and chemical relationships in the epidote- and piemontite-bearing schists suggest a complex metamorphic history for these parageneses, both in the timing of their formation and in the number of interrelating controls that determined their development. Except for the veins that contain abundant quartz + epidote/piemontite, these rocks show little Mn enrichment. Textural evidence suggests that piemontite and epidote, tremolite, spessartine, and the micas grew at all stages of metamorphism with respect to shearing and deformation and hence may be related to both regional and thermal metamorphic events. Chlorite and calcite were restricted to the later part of the metamorphic sequence. The deformational history of the roof pendant has not yet been completely elucidated by radiometric dating and detailed structural mapping; however, gross field relations indicate that most shearing and extension took place during regional metamorphism prior to batholithic intrusion. Hence it may be concluded that some of the Mn-bearing silicates formed during regional metamorphism, with anomalously high f_{O_2} and moderate Mn supply imposed by original bulk rock compositions and mineralogy.

The quartz + piemontite veins near the lower contact with the epidote-bearing mafic rocks and most of the crosscutting epidote- and chlorite-bearing quartz veins may be related to late hydrothermal effects or local remobilization of Mn + SiO_2 associated with faulting or with intrusion of the granitic rocks. Compositionally, these quartz-piemontite veins do concentrate some manganese. The increasingly greater development of piemontite veins along strike toward the intrusive contact further substantiates at least local effects of hydrothermal solutions. However, if significant amounts of such Mn-rich fluids had permeated the country rocks away from the veins as Mayo (1932) suggested, both epidote and piemontite units would have been affected. Also, by the time such hydrothermally-derived fluids were capable of percolating through these rocks, most of the piemontite was already crystallized.

Although metamorphic minerals crystallized through a considerable span of regional and thermal metamorphism and during later hydrothermal activity, both the number of phases and a scarcity of reaction textures suggest that equilibrium may have been maintained. The later hydrothermal effects may have been less strictly controlled by the oxidation state of the rocks themselves; for the most part, however, the pressures, temperatures, and oxygen fugacities probably remained constant in any given horizon throughout the extended metamorphic process, promoting continuous growth of approximately the same mineral assemblage.

Metamorphic grade.—Estimation of metamorphic grade on the basis of the mineral assemblages in these rocks is not straightforward due to the unusual mineral compositions imposed by high oxygen fugacity. Despite the scatter of analyzed feldspar compositions, it appears that albite was the stable metamorphic plagioclase. The characteristic greenschist facies amphiboles are members of the tremolite–actinolite solid solution series; entrance into the albite-epidote amphibolite facies is usually marked by appearance of a more aluminous blue-green hornblende. The stable amphibole through all stages of metamorphism in these rocks was an atypical Mg-rich tremolite. Mg raises the thermal stability of actinolite considerably, as shown by experimental studies by Boyd (1959), Hellner and Schürmann (1966), and Ernst (1968). In addition, the high Mg/Fe ratio imposed by high oxygen fugacity conditions could also have prohibited the formation of hornblende. Hornblende coexisting with actinolite generally shows higher Fe/Mg (Klein, 1969; Brady, 1974). This suggests that crystal chemical controls leading to partitioning of Mg preferentially into actinolitic amphiboles might also delay the appearance of hornblende, if Mg rather than Fe were the most readily available divalent ion.

Huber and Rinehart (1965) suggested that the metavolcanic rocks in the Ritter Range pendant belong to the greenschist facies and noted an increase in metamorphic grade and more complete recrystallization proceeding northwest along strike. Tobisch and others (1977) and Fiske and others (1977) placed the rocks tentatively within the epidote–amphibolite facies. The rocks, mineralogically, belong to the greenschist facies. However, due to the high oxygen fugacity during metamorphism and resulting compositional peculiarities, such mineral assemblages may have persisted to higher temperatures and/or pressures than are usual for greenschist facies rocks.

CORRELATION WITH EXPERIMENTAL DATA

In the case of the Shadow Creek rocks, the unusual Mg-rich mineral compositions assist in correlation between experimentally-derived stability studies and the conditions of formation for the mineral assemblages. A petrogenetic grid showing relevant reaction curves from experimental studies is shown in figure 4, providing us with a check for consistency among the various experimentally-derived physical conditions. In deference to the important role of oxygen fugacity in these rocks, the plot is shown in terms of f_{O_2} versus temperature. The 2 kb phase relations are shown because of the availability of data at this fluid pressure. Regional metamorphism of these rocks may have involved deeper burial and higher pressures, as Bateman and Wahrhaftig (1966)

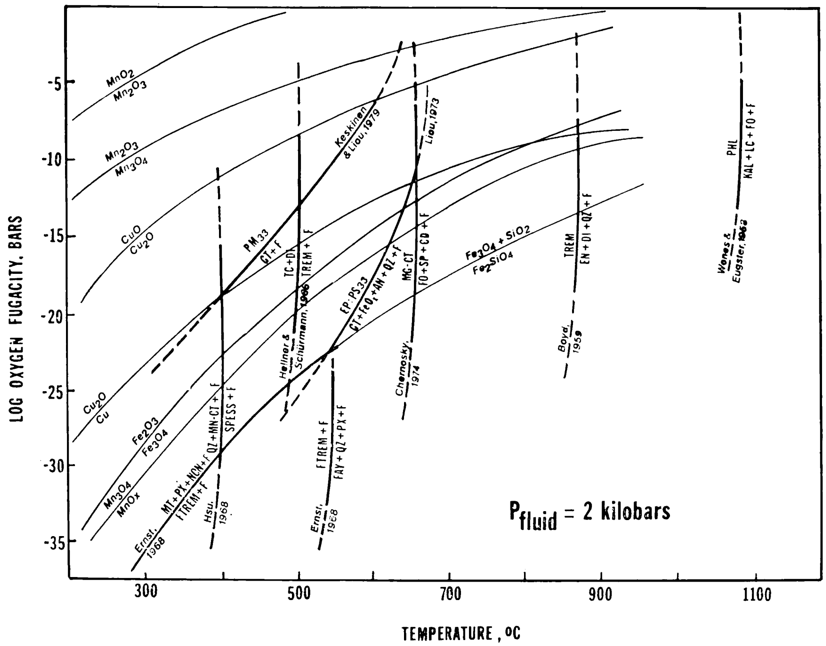

Fig. 4. Experimentally determined mineral equilibria applicable to the Shadow Lake metavolcanic rocks.

PM33: piemontite ($Ca_2MnAl_2Si_3O_{12}(OH)$); EP:PS33: epidote ($Ca_2FeAl_2Si_3O_{12}(OH)$).

AN: anorthite; CD: cordierite; DI: diopside; EN: enstatite; F: fluid; FAY: fayalite; FO: forsterite; FTREM: ferrotremolite; GT: garnet; KAL: kalsilite; LC: leucite; MG-CT: clinochlore; MN-CT: Mn-chlorite; MT: magnetite: NON: nontronite; PHL: phlogopite; PX: pyroxene; QZ: quartz; SP: spinel; SPESS: spessartine; TC: talc; TREM: tremolite.

Buffer curves from Huebner (1971) and Kurshakova, (1971).

estimated 4 to 7.6 kb corresponding to depths of 15 to 27 km. Estimation of metamorphic temperatures at $P_{fluid} = 2$ kb may still be applicable as a check for internal consistency, especially if one considers that some of the piemontite may have recrystallized later, possibly during lower pressure stages of metamorphism.

Stability limits for tremolite (Boyd, 1959; Hellner and Schürmann, 1966), spessartine (Hsu, 1968), clinochlore (Chernosky, 1974), and phlogopite (Wones and Eugster, 1958), shown in figure 4, give approximate temperatures to which these minerals are stable, although the specified reactions may not be those involved in their formation in these rocks. Addition of iron to tremolite and phlogopite markedly lowers their thermal stability limits (Ernst, 1968; Wones, 1958). Similarly, the presence of excess SiO_2 in the system dramatically lowers the breakdown temperatures of chlorite and phlogopite (Chernosky, 1978; Wones and Eugster, 1958).

Until recently, any quantitative information involving piemontite stability had to be obtained from field observations or by analogy with experiments done on the Fe-bearing epidotes (Holdaway, 1972; Liou, 1973). Stability studies at 7 and 15 kb for a range of piemontite compositions (Anastasiou and Langer, 1976, 1977) and at 1 and 2 kb for the Mn-Al "end-member" composition (Keskinen and Liou, 1979a) corroborate evidence from natural piemontite-bearing parageneses that the stability of piemontite is enhanced by high oxygen fugacity (fig. 4). Pure Mn-Al piemontite breaks down to garnet + fluid at 400°C along the copper-cuprite buffer; however, increasing f_{O_2} to that defined by the cuprite–tenorite buffer raises its stability to 617°C at 2 kb. Yellow-green epidote, on the other hand, is stable to higher temperatures (about 645°C) along the copper-cuprite buffer. Addition of Fe^{+3} to piemontite extends its stability to slightly higher temperatures and lower oxygen fugacities. Stability studies for the bulk composition $Ca_2Al_2Mn_{0.5}Fe_{0.5}Si_3O_{12}(OH)$ show breakdown of Fe-bearing piemontite and quartz to garnet + anorthite + fluid along the cuprite–tenorite buffer at 645°C at 2 kb and 477°C along the copper-cuprite buffer (Keskinen and Liou, 1979b).

From partitioning relations described in the previous section, it was concluded that most iron was present as Fe^{+3} during metamorphism and that Mn^{+3}/Mn^{+2} was variable, with this ratio higher in the piemontite rocks than in the epidote units. Therefore, the f_{O_2} range can be estimated as between the HM and Mn_3O_4–Mn_2O_3 buffer curves in figure 4. It is reasonable, then, to postulate that both the piemontite- and epidote-bearing rocks were subjected to an identical temperature (for argument's sake, 500° ± 10°C); the appearance of piemontite or epidote in the different units would then be a function of variations in oxygen fugacity. If f_{O_2} conditions in the piemontite units were near those of the cuprite–tenorite buffer and in the epidote units near the lower copper-cuprite buffer, the observed mineral assemblages would be consistent with the experimental data. Oxygen fugacity would thus have an important effect on Fe^{+3}/Mn^{+3} in the resulting epidote mineral; bulk rock chemistry would, of course, also influence this ratio. Estimates for temperatures for the boundary between the greenschist and amphibolite facies are consistent with the temperature range suggested by the experimentally-determined mineral stabilities, according to a model which assumes f_{O_2} conditions of the CC (or HM) buffer for the epidote units and near the CT buffer for the piemontite units. Turner (1968) and Miyashiro (1973) schematically place the upper limit of the greenschist facies at 350° to 450°C. Experimental investigation of this boundary using hydrothermal techniques and basaltic bulk compositions by Liou, Kuniyoshi, and Ito (1974) delineated a transitional zone between greenschist and amphibolite facies at 475° to 550°C.

DISCUSSION OF OXYGEN FUGACITY

A fundamental question remains: what was the origin and mechanism involved in creating and maintaining the unusually high oxidation state in these rocks? Why was f_{O_2} higher (if only marginally) in the piemontite rocks than in the epidote rocks? Examination of the Fe^{+2}/Fe^{+3} ratios for igneous rocks shows a general increase in degree of oxidation from mafic toward more felsic rocks (Mueller, 1970; Landergren, 1975). The piemontite units are notably more silicic than the epidote-bearing rocks; in accordance with this trend, the piemontite units should, as observed, be somewhat more oxidized. The mechanism of emplacement may also have contributed to the oxidation of the crystal and lithic tuffs. Comparison of Fe_2O_3/FeO ratios for otherwise genetically and chemically similar obsidian glasses from several localities indicates generally higher oxidation for pumiceous rocks than for glassy flows (Shepherd, 1938). Susceptibility to immediately post-depositional surface processes is undoubtedly greater for disaggregated or slightly welded ash deposits than for massive flows. Soil formation, or more likely, extensive submarine weathering in an oxygenated environment with concurrent chert and pyrolusite deposition during a period of declining volcanic activity, could also account for both the higher degree of oxidation and the silica enrichment observed in the piemontite-bearing units (M. Holdaway, personal commun.).

Transition metals, predominantly Mn and Fe, exert the dominant control on oxygen fugacity in lithologic units not open to external buffering. Permeability (due to original pore space) doubtless decreases, except for the effects of later shearing, during compaction and metamorphism, hence the scale of fluid-solid equilibrium would become progressively more local and more strictly controlled by the existing mineral assemblage (and perhaps more resistant to change) as metamorphism proceeds. From textural evidence, it appears that a very fine-grained matrix of quartz + feldspar + hematite resulted from the rapid devitrification of the tuffaceous glass, effectively "locking" all the Fe in a trivalent state. The oxidized state may have been either inherited from the magma or derived during or shortly after explosive extrusion. Original MnO_2 could also have provided extra buffer capacity to raise the oxygen fugacity in these rocks. Once the fine-grained glass was crystallized to hematite + iron-poor silicates, local f_{O_2} would be maintained; small variations in f_{O_2} between units would be attributable to varying concentrations of Mn^{+4}:Mn^{+3}:Mn^{+2} and perhaps Ti. Without an influx of great quantities of external fluids (an open system), there was no particular impetus towards reduction in these rocks. Once piemontite was formed, the survival of trivalent Mn was further enhanced; indeed the strong crystal field stabilization of Mn^{+3} in the epidote structure may have promoted oxidation of the transition metals above the Mn^{+3}/Mn^{+2} ratios existing in the equilibrium fluid, once a certain threshold stability was attained. Smith and Albee (1967) note that due to this preferential partitioning of ions by phases, ratios of different valences of transition metals in minerals may represent equilibrium but need not necessarily duplicate those present in the fluid during mineral growth.

As the complex sequence of mineral growth and replacement continued, oxygen fugacity of the local metamorphic fluids probably was fixed or oscillated between narrow limits. Fine-grained hematite maintained the dominance of Fe^{+3}; oxidized mineral assemblages also cooperated in buffering the fluid and controlled the formation of compositionally similar phases. Hence both early piemontite and tremolite and later grains of these same minerals perpetuated nearly identical compositions. In the epidote-bearing rocks, lower initial Fe^{+3}/Fe^{+2} and Mn^{+4}+ Mn^{+3}/Mn^{+2} maintained f_{O_2} closer to the Fe_2O_3–Fe_3O_4 buffer curve, or perhaps the effect of Ca on the original titaniferous hematites, promoting the growth of sphene, undermined the persistence of hematite to some extent. Much of the green epidote may also represent replacement of original ferrous silicates in the flows.

Occurrences of similar interbedded piemontite- and epidote-bearing zones, indicative of limited communication of metamorphic fluids between adjacent strata, have been described by Smith and Albee (1967) and Gresens and Stensrud (1974, 1977). The importance of oxidation-reduction reactions in geologic processes and their influence on mineral stabilities have long been recognized; the complex interaction between fluid composition, mineral stability, and crystal chemistry has not necessarily been fully assessed.

CONCLUSIONS

The metavolcanic piemontite- and epidote-bearing units of the Shadow Lake area exhibit evidence of an extended cycle of pre- to post-tectonic crystallization under conditions transitional between the greenschist and epidote-amphibolite facies. All units show mineralogical and chemical indications of unusually high oxygen fugacity (10^{-20}-10^{-10} bars at P_{fluid} = 2kb and T = 450°-550°C), well within the hematite stability field during metamorphism. Cation partitioning of the coexisting phases suggests that somewhat higher f_{O_2} permitted the growth of piemontite rather than green epidote in the lithic and crystal tuffs of the piemontite zone. Bulk compositional differences between the andesitic to basaltic epidote-bearing lavas and the rhyolitic to dacitic crystal tuffs have a significant but secondary effect on the stable mineral compositions. Imposition of high f_{O_2} conditions can be attributed primarily to local buffering controls related to the sequence of metamorphism, beginning with the premetamorphic state of the rocks. Early devitrification of the glassy tuffaceous units led to stabilization of quartz + plagioclase + hematite in the groundmass. The predominance of hematite exerted a prevailing influence throughout the subsequent metamorphism by maintaining, along with fairly high $Mn^{+3}+Mn^{+4}/Mn,^{+2}$ a high f_{O_2}.

Unusually Mg-rich muscovite, phlogopite, tremolite, and chlorite suggest metamorphism under conditions of high oxygen fugacity. High Mn/Fe in minerals requiring divalent transition metals suggest a fluid phase rich in Fe^{+3} but in which the Mn was still dominantly divalent, a condition consistent with the higher oxidation potential of Mn than Fe.

The piemontite-bearing rocks, although characterized by a variety of fairly manganese-rich minerals, have bulk compositions that do not suggest extensive Mn enrichment with respect to "normal" metavolcanic rocks or to adjacent epidote-bearing metavolcanics. Local hydrothermal mobilization, which resulted in later quartz + piemontite veins, may represent a relatively minor contribution associated with faulting and/or emplacement of the Sierra Nevada batholith. The metamorphic sequence in the Shadow Lake region is complex both in the number of episodes of mineral growth and in the number of variables affecting the resultant mineralogy, emphasizing the interrelationships between mineral stability, crystal chemistry, and physico-chemical conditions of metamorphism.

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