

## Cuprian manganooan phlogopite in highly oxidized Mineoka siliceous schists from Kamogawa, Boso Peninsula, central Japan

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### ABSTRACT

Phlogopite occurring sparsely in highly oxidized siliceous schists of the Mineoka metamorphic rocks contains up to 5.5 wt% CuO and up to 7.5 wt% MnO. The phlogopite coexists with albite, microcline, quartz, hematite, apatite  $\pm$  manganooan aegirine augite, tirodite, piemontite, spessartine, and calcite. Sulfide minerals are absent. The manganooan aegirine augite and tirodite close to the phlogopite also contain small amounts of Cu, up to 0.2 and 0.6 wt% CuO, respectively. In addition, most ferromagnesian silicates and hematite may contain small to substantial amounts of Mn<sup>3+</sup>. Metamorphic conditions are estimated to be  $\log f_{\text{O}_2} = -6.5 \pm 2$  at  $\sim 550$  °C. Cu<sup>2+</sup> substitutes for Mg<sup>2+</sup> in octahedral sites in phlogopite and, less extensively, other ferromagnesian silicate minerals under relatively oxidizing conditions where  $f_{\text{S}_2}$  is sufficiently low for chalcopyrite to be unstable. The preferential incorporation of Cu<sup>2+</sup> along with Mn<sup>3+</sup> in phlogopite may be due to the cooperative Jahn-Teller effects of these cations and the chemically anisotropic property of the octahedral sites in phlogopite.

### INTRODUCTION

Cu-bearing biotite has been known to occur in and around copper deposits (e.g., Parry and Nackowski, 1963; Lovering, 1969; Al-Hashimi and Brownlow, 1970; Lovering et al., 1970; Graybeal, 1973; Kesler et al., 1975; Mason, 1978; Hendry et al., 1981, 1985) and in other ordinary paragneisses (e.g., Annersten and Ekström, 1971; Gresens and Stensrud, 1971, 1974). Using the transmission electron microscope, Ilton and Veblen (1988) found submicroscopic particles of native copper incorporated between sheets of biotite in magnetite-bearing rocks. Although this mode of occurrence of native copper is unexpected, it is consistent with stability relations of metallic Cu. If  $f_{\text{S}_2}$  is low enough, metallic Cu is stable with magnetite at temperatures below ca. 700 °C (e.g., Yund and Kullerud, 1964). Cu<sup>2+</sup> would be incorporated in oxide and silicate minerals at higher  $f_{\text{O}_2}$  corresponding to the stability field of hematite. Finger et al. (1989) reported alkaline-earth copper silicates formed in open silica boats as by-products of the search for superconductors.

A variety of metamorphic rocks occur in the Mineoka tectonic zone of the Boso Peninsula, central Japan. They are mostly oxidized, as indicated by the widespread occurrence of hematite and by the chemical compositions of minerals such as amphibole and pyroxene. A few siliceous schists contain Cu<sup>2+</sup>-rich phlogopite and Cu<sup>2+</sup>-bearing manganooan aegirine augite and tirodite.

The purpose of this paper is to present petrographic and mineral chemical data for the cuprian manganooan phlogopite-bearing siliceous schists. We conclude that Cu<sup>2+</sup> substitutes for Mg<sup>2+</sup> in the octahedral sites in phlog-

opite and other ferromagnesian silicate minerals under highly oxidizing conditions.

### GEOLOGICAL SETTING

The Mineoka metamorphic rocks usually occur as tectonic blocks within sheared serpentinites (e.g., Kanehira et al., 1968; Ogawa and Taniguchi, 1988; Ogo and Hiroi, 1991). The metamorphic rocks under consideration here form a shore reef, about 20  $\times$  10 m in size, near the Kamogawa fishing port (Fig. 1). They are mostly basic schists, in which siliceous and psammitic schists constitute a thin layer up to 30 cm in thickness (Fig. 1). These metamorphic rocks were extensively fractured into breccias during movements within the serpentinites after the peak of metamorphism (ca. 38 Ma; Yoshida, 1974; Hiroi et al., in preparation). Nevertheless, the thin layer composed of siliceous and psammitic schists is traceable from one edge of the block to the other (Fig. 1), and the original concordant and gradual lithostratigraphic relations between the different rock types are well preserved in some cases (Ogo and Hiroi, 1991). Ogo and Hiroi (1991) presented detailed petrography and mineral chemistry of the rocks and discussed the origin of various mineral assemblages (see Table 1). They pointed out that metamorphic grade is transitional between the epidote amphibolite and the amphibolite facies and that a wide range of oxidation state in the rocks, probably established during sedimentation, played an important role in determining the assemblages and compositions of minerals. They also estimated peak metamorphic conditions to be  $\sim 550$  °C and ca. 5 kbar based on the mineral assemblages in basic

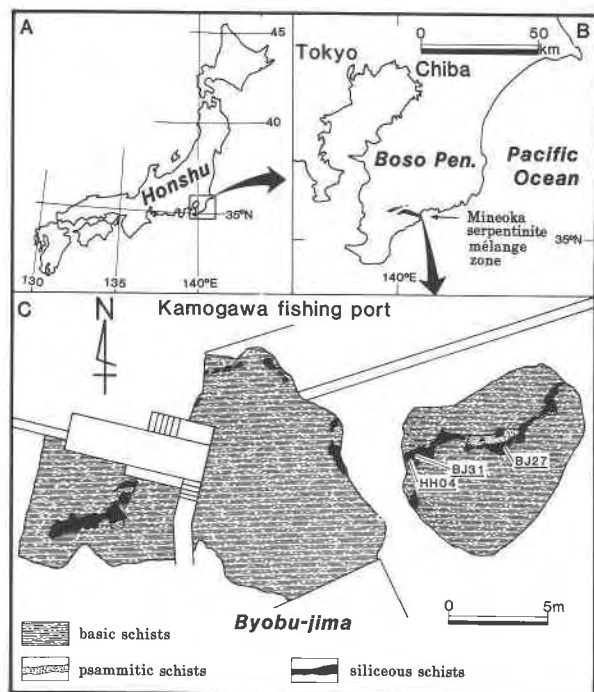


Fig. 1. Localities of Mineoka serpentinite-mélange zone and metamorphic rocks including siliceous schists that contain cuprian manganous phlogopite. (A), (B) Locality of the Mineoka serpentinite-mélange zone. (C) Sketch map of the metamorphic rocks at Kamogawa, showing locations of samples.

schists and the magnitude of the jadeite component in clinopyroxenes in both basic and siliceous schists.

#### PETROGRAPHY OF CUPRIAN MANGANOAN PHLOGOPITE-BEARING SILICEOUS SCHISTS

The cuprian manganous phlogopite-bearing and associated siliceous schists may be derived from cherts because they show a finely laminated structure (Fig. 2). A small amount of cuprian manganous phlogopite has been found in some aegirine augite-bearing rocks. It occurs in thin layers, up to 2 mm thick, alternating with layers richer in hematite, aegirine augite, amphibole, or Cu-poor phlogopite (Fig. 2B). It is usually present as fine-grained flakes, up to 0.1 mm long, sporadically scattered among dominant quartz grains (Figs. 2C, 2D). Small amounts of fine-grained aegirine augite, tirodite, piemontite, spessartine, hematite, albite, microcline, calcite, and apatite also occur sparsely among quartz grains (Figs. 2A, 2C, 2D). These minerals are locally in direct contact with each other. Hematite is the only iron oxide present in the cuprian manganous phlogopite-bearing rocks and is free of ilmenite lamellae as seen under the microscope. No sulfide minerals have been found in the rocks.

Cuprian manganous phlogopite has a bronze tint, but it is difficult to distinguish from Cu-poor brownish phlogopite under the microscope. Aegirine augite has a brownish yellow tint and often shows anomalous interference

color. Prismatic tirodite is virtually colorless. Spessartine is pale yellow and rarely shows weak optical anisotropy.

#### CHEMICAL COMPOSITIONS OF MINERALS IN THE SCHISTS

Minerals were analyzed with an energy-dispersive Hitachi scanning electron microscope S550 equipped with a Kevex X-ray analytical system. Metallic Cu was used as the standard for Cu. Data were processed by the method developed by Mori and Kanehira (1984). At least one to four spots were analyzed per grain of phlogopite and other minerals. Selected analyses are listed in Tables 2–6.

**Phlogopite.** The chemical composition of phlogopite, especially Cu-rich material, is highly variable from grain to grain, but each grain is homogeneous. Moreover,  $K_2O$  contents of the analyzed phlogopite are usually more than 9 wt%, indicating that they are free of chlorite and vermiculite alteration (cf. Veblen and Ferry, 1983; Brindley et al., 1983). The phlogopite contains up to 5.5 wt% CuO and up to 7.5 wt% MnO. Cu varies inversely with Mg and with (Mg + Mn) but increases with Mn (Fig. 3). Some Mn in the phlogopite may be  $Mn^{3+}$  because  $Mn^{3+}$  is inferred to be present in the coexisting manganous aegirine augite, tirodite, and hematite (see below) and because a relatively large amount of  $Mn^{3+}$  has been reported for manganous phlogopite in similarly or less oxidized rocks from the Nodatamagawa mine, Japan (Kato et al., 1979). Phlogopite in direct contact with spessartine is depleted in Mn compared with other phlogopite (Fig. 3), suggesting either lower  $Mn^{3+}/Mn^{2+}$  ratios in phlogopite compared with those in the spessartine-free specimens or local Mg-Mn<sup>2+</sup> exchange upon cooling. Ba, S, and Cl have not been detected in these phlogopite samples. A careful search for particles of Cu metal or copper(-iron) sulfide in these phlogopite samples was carried out, using two different scanning electron microscopes at Chiba University and the National Science Museum in Tokyo, but none were found (cf. Ilton and Veblen, 1988).

**Aegirine augite.** The chemical composition of aegirine augite also varies from grain to grain in the same thin layer. It contains variable amounts of Na and Mn. A complementary relationship between (Ca + Na) and Mn is seen in addition to that between Ca and Na, indicating that Mn tends to enter the M2 site. However, some of the Mn must be in the M1 site. Calculations based on stoichiometry suggest that most Fe may be  $Fe^{3+}$  and that some Mn is possibly  $Mn^{3+}$ . Less than 10 mol% jadeite component is present in these aegirine augite samples. A few grains occurring close to cuprian manganous phlogopite contain up to 0.2 wt% CuO.

**Amphibole.** Amphiboles in the aegirine augite-bearing siliceous schists include sodic-calcic, alkali, and Fe-Mg-Mn varieties (Ogo and Hiroi, 1991). The amphibole coexisting with cuprian manganous phlogopite is tirodite containing up to 17 wt% MnO. Most of the Mn may be  $Mn^{2+}$  in the B site (terminology of Leake, 1978), as pointed out by Klein (1964), but part of the Mn, probably as  $Mn^{3+}$ , could be in the C site as suggested by Nambu et al. (1980) and Hashimoto et al. (1990). Some grains oc-

TABLE 1. Mineral assemblages of Mineoka metamorphic rocks from Kamogawa

Rock type	Mineral assemblage
Basic	B-1: Hbl + Ep + Pl* + Qtz + Spn + Rt + Hem** + Ap ± Cal ± Ccp B-2: Hbl + Pl† + Qtz + Spn + Rt + Ilm + Cal + Po + Ap ± Ep B-3: Hbl + Grt + Ep + Ab + Qtz + Spn + Hem + Ap B-4: Hbl + Aug + Ep + Ab + Qtz + Spn + Hem + Ap B-5: Act, Hbl + Ep + Ab + Spn + Rt + Cal + Ap B-6: Act, Hbl + Ep + Qtz + Spn + Rt + Cal + Ap B-7: Act + Ep + Spn + Rt + Cal + Ap
Siliceous	S-1: Agt + Int. Am + Phl + Ab + Kfs + Qtz + Hem + Ap ± Pmt ± Cal S-2: Agt + Grt + Phl + Ab + Kfs + Qtz + Hem + Ap ± Int. Am ± Pmt ± Cal S-3: Agt + Grt + Int. Am + Ab + Kfs + Qtz + Mag + Hem + Ap S-4: Ep + Grt + Act + Qtz + Hem + Cal + Ap S-5: Ep + Act + Phl + Qtz + Hem + Cal + Ap S-6: Ep + Phl + Ab + Qtz + Hem + Ap ± Ms
Psammitic	Ep + Phl + Ms + Pl* + Kfs + Qtz + Hem + Ap + Zrn (+ Atc + Ccp)‡

Note: Mineral abbreviations are as follows. Ab = albite; Act = actinolite; Agt = aegirine augite; Ap = apatite; Atc = atacamite; Aug = augite; Cal = calcite; Ccp = chalcopyrite; Ep = epidote; Grt = garnet; Hem = hematite; Hbl = hornblende; Ilm = ilmenite; Kfs = potassium feldspar; Mag = magnetite; Ms = muscovite; Phl = phlogopite; Pl = plagioclase; Pmt = piemontite; Po = pyrrhotite; Qtz = quartz; Rt = rutile; Spn = sphene; Zrn = zircon; Act, Hbl = actinolitic hornblende (Arai and Hirai, 1985); Int. Am = Ca-Na-(Fe,Mg,Mn) intermediate amphibole including riebeckitic tirodite.

\* An 0-13.

\*\* With ilmenite lamellae.

† An 10-33.

‡ In granitic pebble.

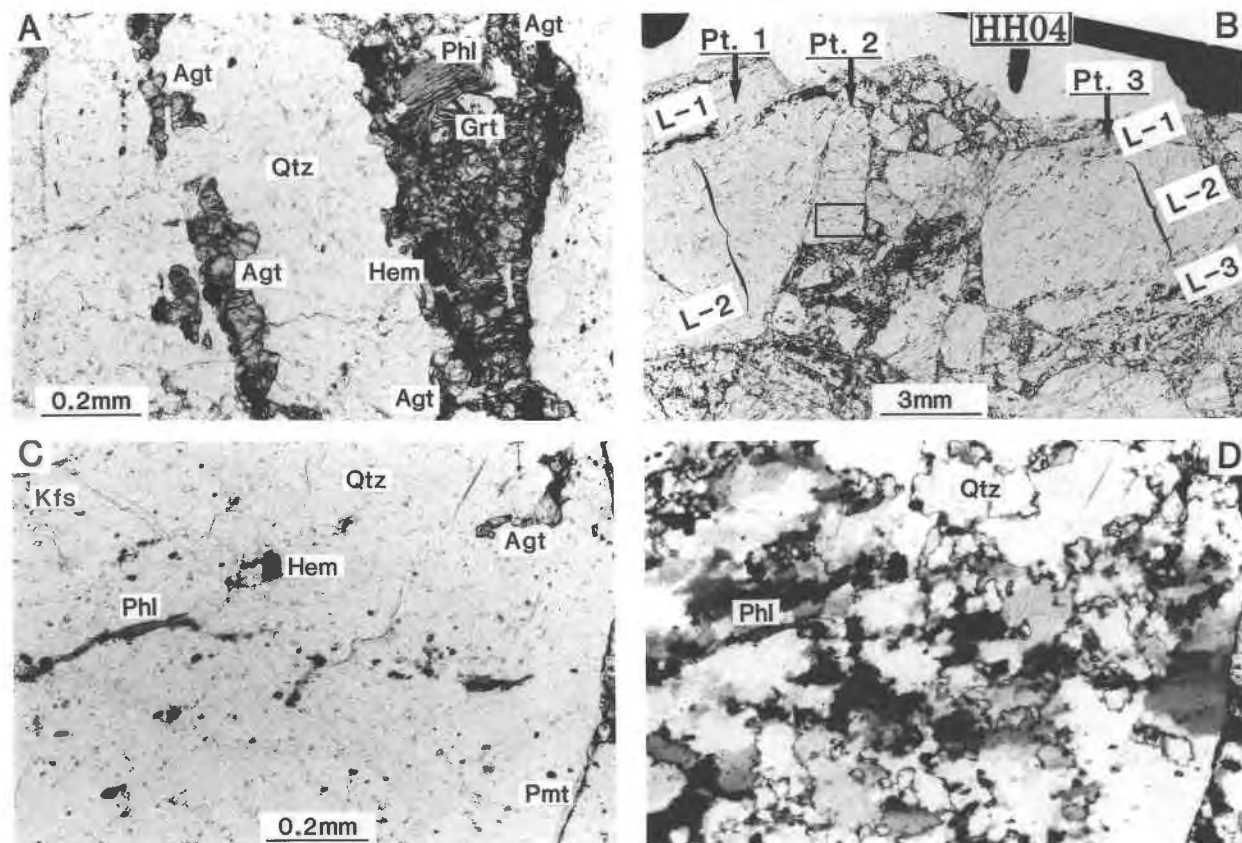


Fig. 2. Photomicrographs of Mineoka siliceous schists containing cuprian manganian phlogopite. (A) Cuprian manganian phlogopite coexisting with spessartine, aegirine augite, and hematite in BJ31. Microcline is also present (plane polarized light). (B) Brecciated siliceous schist (HH04) with cuprian manganian phlogopite-bearing parts 1-3 (Pt. 1-Pt. 3). Parts 1 and 3 show layering, and cuprian manganian phlogopite occurs only in layer

2 (L-2) (plane polarized light). (C), (D) Photomicrographs of the enlarged area in the rectangle in B, showing sparse occurrence of fine-grained cuprian manganian phlogopite, manganian aegirine augite, piemontite, and hematite among dominant, relatively coarse-grained quartz. (C) Plane polarized light, (D) crossed polars.

TABLE 2. Selected analyses of phlogopite

Sp. no.	BJ27		BJ31		HH04						
	1	1	1	1	1	1	1	2	2	2	3
Part	1	1	2	1	1	1	2	2	2	2	3
Min. assem.	S-1	S-2	S-1	S-1	S-1	S-1	S-1	S-1	S-1	S-1	S-1
SiO <sub>2</sub>	39.85	39.47	40.04	39.30	41.32	41.57	39.28	38.74	41.18	40.81	
TiO <sub>2</sub>	1.07	1.20	1.35	0.79	1.36	0.90	1.16	0.94	1.42	1.05	
Al <sub>2</sub> O <sub>3</sub>	12.57	11.83	12.54	12.90	12.90	12.37	12.14	11.59	12.09	13.63	
Fe <sub>2</sub> O <sub>3</sub> *	3.67	3.06	3.75	4.44	3.70	2.94	3.85	4.48	3.40	4.38	
MnO**	5.30	4.52	5.74	7.30	4.55	4.36	5.95	7.34	5.02	4.84	
NiO	—	0.21	—	0.14	—	—	—	0.04	0.14	—	
CuO	1.65	3.76	2.17	4.88	0.16	1.29	4.04	5.42	1.55	0.64	
MgO	19.43	18.97	18.83	15.01	20.23	20.63	16.77	14.81	19.29	19.64	
CaO	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	
K <sub>2</sub> O	10.32	9.99	9.90	10.29	10.67	10.82	10.36	9.60	10.60	10.21	
Total	93.86	92.98	94.32	95.05	94.89	94.88	93.54	92.96	94.70	95.20	
					O = 22						
Si	5.886	5.925	5.896	5.901	5.957	6.017	5.927	5.962	6.010	5.883	
Ti	0.119	0.136	0.150	0.089	0.148	0.098	0.131	0.108	0.156	0.114	
Al	2.188	2.093	2.176	2.283	2.193	2.110	2.160	2.101	2.080	2.316	
Fe <sup>3+</sup> *	0.408	0.345	0.416	0.502	0.401	0.321	0.437	0.519	0.374	0.475	
Mn <sup>2+</sup> **	0.663	0.575	0.715	0.929	0.556	0.534	0.760	0.957	0.620	0.591	
Ni	—	0.025	—	0.017	—	—	—	0.005	0.016	—	
Cu	0.184	0.422	0.241	0.553	0.017	0.141	0.460	0.630	0.171	0.070	
Mg	4.277	4.244	4.133	3.359	4.347	4.451	3.771	3.396	4.196	4.219	
Ca	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	
K	1.944	1.913	1.860	1.971	1.962	1.997	1.994	1.884	1.972	1.878	
Total	15.669	15.678	15.587	15.604	15.581	15.669	15.640	15.562	15.595	15.546	

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.

\*\* Total Mn as MnO.

curing close to cuprian manganian phlogopite contain up to 0.6 wt% CuO and up to 0.2 wt% ZnO. In addition, a small amount of Ni is occasionally found in these amphiboles. Arai and Hirai (1986) reported Ni-bearing sodic-calcic amphiboles in some other siliceous schists from the same locality.

**Hematite.** The chemical composition of hematite varies significantly from layer to layer in the same thin sec-

tion (see Fig. 2B, Table 6), indicating distinctly different oxidation conditions between the cuprian manganian phlogopite-bearing thin layer and others. Hematite occurring in the cuprian manganian phlogopite-bearing thin layer contains up to 3 wt% MnO and 1.7 wt% TiO<sub>2</sub>. Stoi-

TABLE 3. Selected analyses of aegirine augite

Sp. no.	BJ31		HH04		
	1	1	1	2	3
Part	1	1	1	2	3
Min. assem.	S-2	S-1	S-1	S-1	S-1
SiO <sub>2</sub>	53.19	53.68	53.52	53.25	52.73
Al <sub>2</sub> O <sub>3</sub>	2.06	0.98	2.12	1.33	1.57
Fe <sub>2</sub> O <sub>3</sub> *	11.48	17.11	11.51	15.44	14.97
MnO**	7.44	6.77	3.51	5.79	4.89
CuO	—	—	—	0.17	—
MgO	8.48	6.86	9.69	7.19	7.76
CaO	11.02	8.55	14.89	9.63	10.54
Na <sub>2</sub> O	5.85	7.48	5.28	6.90	6.79
Total	99.53	101.42	100.52	99.69	99.25
			O = 6		
Si	2.002	2.003	1.979	2.009	1.993
Al	0.091	0.043	0.093	0.059	0.070
Fe <sup>3+</sup> *	0.325	0.480	0.320	0.439	0.426
Mn <sup>2+</sup> **	0.237	0.214	0.110	0.185	0.157
Cu	—	—	—	0.005	—
Mg	0.476	0.382	0.534	0.404	0.437
Ca	0.445	0.342	0.590	0.389	0.427
Na	0.427	0.541	0.378	0.505	0.498
Total	4.003	4.005	4.004	3.995	4.008

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.

\*\* Total Mn as MnO.

TABLE 4. Selected analyses of amphibole

Sp. no.	HH04				
	1	1	1	3	3
Part	1	1	1	3	3
Min. assem.	S-1	S-1	S-1	S-1	S-1
SiO <sub>2</sub>	55.79	56.20	56.21	55.15	55.71
Al <sub>2</sub> O <sub>3</sub>	0.51	0.34	0.55	0.11	0.17
Fe <sub>2</sub> O <sub>3</sub> *	3.25	2.41	3.04	1.33	2.61
MnO**	14.61	15.86	15.07	16.97	14.58
NiO	—	—	0.14	—	—
CuO	—	—	0.61	0.44	—
ZnO	—	—	0.07	—	—
MgO	18.97	19.55	18.74	19.01	19.63
CaO	1.57	1.62	1.64	1.29	1.86
Na <sub>2</sub> O	1.84	1.59	1.84	1.31	1.64
Total	96.53	97.57	97.91	95.61	96.20
			O = 23		
Si	8.007	8.000	7.996	8.044	8.016
Al	0.087	0.057	0.092	0.019	0.029
Fe <sup>3+</sup> *	0.351	0.259	0.326	0.146	0.283
Mn <sup>2+</sup> **	1.776	1.912	1.815	2.096	1.777
Ni	—	—	0.016	—	—
Cu	—	—	0.066	0.049	—
Zn	—	—	0.008	—	—
Mg	4.058	4.149	3.974	4.133	4.209
Ca	0.241	0.248	0.250	0.201	0.287
Na	0.511	0.439	0.507	0.370	0.457
Total	15.031	15.064	15.050	15.058	15.058

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.

\*\* Total Mn as MnO.

TABLE 5. Selected analyses of garnet and piemontite

Sp. no.	Grt		Piemontite	
	BJ31	BJ31	HH04	HH04
Part	1	1	2	2
Min. assem.	S-2	S-2	S-1	S-1
SiO <sub>2</sub>	36.25	36.79	36.94	—
TiO <sub>2</sub>	0.27	—	—	—
Al <sub>2</sub> O <sub>3</sub>	15.83	18.63	18.29	—
Fe <sub>2</sub> O <sub>3</sub> *	6.65	8.34	9.65	—
Mn <sub>2</sub> O <sub>3</sub> **	—	10.60	10.42	—
MnO†	36.00	—	—	—
MgO	0.41	—	—	—
CaO	4.85	22.85	22.15	—
Total	100.21	97.21	97.44	—
O	12	25	25	—
Si	3.008	6.030	6.470	—
Ti	0.013	—	—	—
Al	1.548	3.599	3.528	—
Fe <sup>3+</sup>	0.415	1.028	1.189	—
Mn <sup>3+</sup> **	—	1.323	1.298	—
Mn <sup>2+</sup> †	2.531	—	—	—
Mg	0.051	—	—	—
Ca	0.431	4.014	3.884	—
Total	7.997	15.995	15.946	—

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.  
 \*\* Total Mn as Mn<sub>2</sub>O<sub>3</sub>.  
 † Total Mn as MnO.

chiometric calculations suggest that some Mn could be Mn<sup>3+</sup> substituting for Fe<sup>3+</sup>. On the other hand, hematite in adjacent thin layers contains up to 1.7 wt% MnO and 2.6 wt% TiO<sub>2</sub>, and the Mn is incorporated only as the pyrophanite component.

**Other minerals.** Garnet in the siliceous schists is spessartine containing subordinate grossular and andradite. Spessartine coexisting with cuprian phlogopite is richer in Fe<sup>3+</sup> (probably as andradite) than spessartine in other siliceous schists.

Piemontite coexisting with cuprian phlogopite contains 20–23 mol% piemontite and 17–20 mol% pistacite components.

Microcline characteristically occurs together with albite in aegirine augite-bearing siliceous schists and usu-

ally contains 1–2 wt% BaO and little Na<sub>2</sub>O. Albite in the siliceous schists is almost pure albite, suggesting that little Ca was available for feldspar. Two-feldspar thermometers (e.g., Stormer, 1975; Brown and Parsons, 1981) yield low temperatures (<300 °C) for the feldspar pairs, suggesting recrystallization upon cooling.

## DISCUSSION AND CONCLUSIONS

Cu<sup>2+</sup> is incorporated in the crystal structure of phlogopite and, together with Mn<sup>2+</sup> and Mn<sup>3+</sup>, substitutes for Mg<sup>2+</sup> in the octahedral sites. This is evident from the inverse relationships between Cu and Mg and between Cu and (Mg + Mn) and the positive correlation between Cu and Mn in Mineoka cuprian manganian phlogopite, whereas the contents of other constituents remain constant (Fig. 3). In addition, a given grain is chemically homogeneous. No Cu metal or sulfide was found between the cleavage sheets. The presence of Cu<sup>2+</sup> in manganian aegirine augite and tirodite associated with the cuprian manganian phlogopite is further evidence that Cu<sup>2+</sup> can be incorporated in ferromagnesian silicates. The relative Cu/Mg ratios of the coexisting phases are phlogopite > amphibole > pyroxene, indicating that Cu<sup>2+</sup> preferentially enters phlogopite.

Schwarzc (1967) and Annersten and Ekström (1971) studied the distribution of Cu and other major and minor elements between coexisting metamorphic minerals, referring to the crystal field stabilization and Jahn-Teller effects of the transition elements in an octahedral site (Orgel, 1960; Burns, 1970). Dunitz and Orgel (1957) pointed out that Cu<sup>2+</sup> and Mn<sup>3+</sup> are stabilized in tetragonally distorted octahedra by the Jahn-Teller effect of their d<sup>9</sup> and d<sup>4</sup> configurations, respectively. Moreover, Wojtowicz (1959) theoretically showed the profound effect of cooperative Jahn-Teller distortions on the phase transformations of spinel minerals. The preferential incorporation of Cu<sup>2+</sup> in phlogopite may be best explained by the chemically anisotropic property of the octahedral sites in phlogopite, bonded to four O atoms and two OH ions.

TABLE 6. Selected analyses of hematite

Sp. no.	BJ27		BJ31		HH04		
	1	1	1	2	1	2	3
Part	1	1	2	1	2	3	3
Layer	—	—	—	2	—	2	3
Min. assem.	S-1	S-2	S-1	S-1	S-1	S-1	S-1
TiO <sub>2</sub>	1.62	1.24	1.52	1.63	1.70	1.42	2.19
Fe <sub>2</sub> O <sub>3</sub> *	96.37	96.97	96.44	95.72	95.41	95.02	97.01
MnO**	1.85	1.70	2.23	1.93	2.21	2.93	1.62
Total	99.84	99.91	100.19	99.28	99.32	99.37	100.82
				O = 3			
Ti	0.032	0.025	0.030	0.033	0.034	0.029	0.043
Fe <sup>3+</sup>	1.926	1.937	1.920	1.924	1.916	1.905	1.914
Mn <sup>3+</sup>	0.010	0.013	0.020	0.011	0.016	0.037	—
Fe <sup>2+</sup>	—	—	—	—	—	—	0.007
Mn <sup>2+</sup>	0.032	0.025	0.030	0.032	0.034	0.029	0.036
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000

\* Total Fe as Fe<sub>2</sub>O<sub>3</sub>.  
 \*\* Total Mn as MnO.

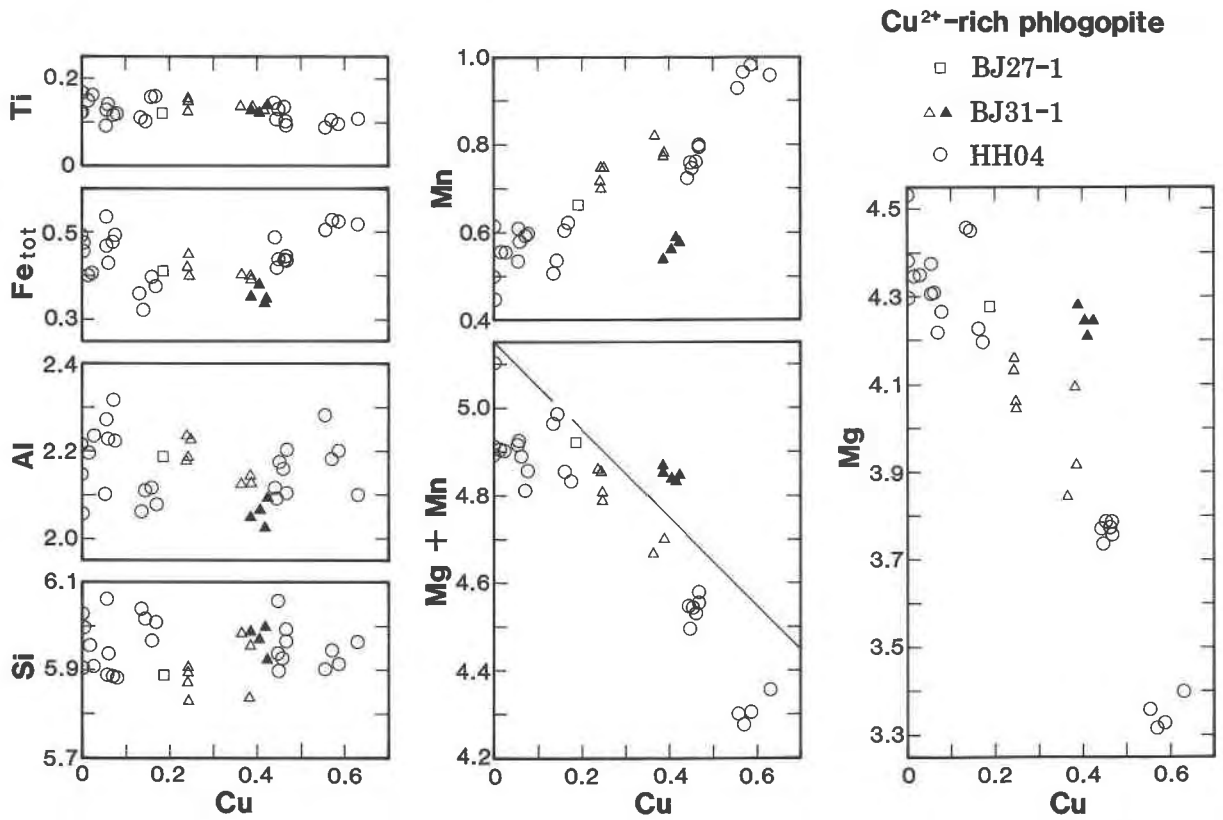


Fig. 3. Plots of Cu vs. other constituents (for O = 22) in individual analyses of cuprian manganoan phlogopites from Mineoka siliceous schists. Solid triangles are analyses of a single grain in direct contact with spessartine, manganoan aegirine augite, and hematite as shown in Figure 2A. Substitution line Cu-(Mg + Mn) is included for reference only.

Hazen and Wones (1972) revealed the linear relationships between ionic radii (Shannon and Prewitt, 1970) and unit-cell edges and between ionic radii cubed and unit-cell volumes of synthetic hydrous trioctahedral micas including cuprian phlogopite. They also showed that octahedral cations of greater than 0.78 Å average ionic radius do not form stable trioctahedral micas of the form of  $KR_3^{2+}AlSi_3O_{10}(OH)_2$  because of the misfit between smaller tetrahedral layers and a larger octahedral sheet (see Bailey, 1984a, 1984b, for more comprehensive discussion). The possible misfit between these layers owing to the incorporation of the relatively large amount of  $Mn^{2+}$  in the Mineoka phlogopite may be negated by the excess  $Al^{3+}$  and  $Fe^{3+}$  in them. Hazen and Wones (1972) reported that  $Mn^{2+}$  mica with excess Al was synthesized, but synthesis of pure  $Mn^{2+}$  phlogopite was not successful.

$Cu^{2+}$  is a constituent of silicate and oxide minerals only at high  $f_{O_2}$  and low  $f_{S_2}$  (e.g., Holland, 1959, 1965). The ferromagnesian minerals in the cuprian manganoan phlogopite-bearing thin layers are rich in Mg and Mn. This is in good agreement with the existing experimental and petrographic data of rocks crystallized under variable oxidation and sulfidation conditions at the same  $P$ - $T$ . Ferromagnesian minerals are depleted in  $Fe^{2+}$  components with increasing  $f_{O_2}$  and  $f_{S_2}$  (e.g., Chinner, 1960;

Mueller, 1960; Froese, 1977; Popp et al., 1977a, 1977b; Tso et al., 1979; Nesbitt, 1986a, 1986b; Tracy and Robinson, 1988). The occurrence of piemontite in some of the cuprian manganoan phlogopite-bearing siliceous schists metamorphosed at  $\sim 550$  °C also indicates conditions as oxidizing as those of the  $Cu_2O + CuO$  buffer (Keskinen and Liou, 1979, 1987). Further evidence of highly oxidizing conditions is the possibility that Mn in excess of that combined with Ti as pyrophanite solid solution in hematite is trivalent. Moreover, possibly primary atacamite [ $Cu_2Cl(OH)_3$ ] sporadically replaces chalcopyrite within some granitic pebbles in nearby psammitic schists, indicating that Cu is divalent in some of the Mineoka metamorphic rocks (Ogo and Hiroi, 1991). On the other hand, the presence of  $Mn^{2+}$  in most of the ferromagnesian minerals indicates conditions that are not so oxidizing as those of the  $Mn_3O_4 + Mn_2O_3$  buffer. Thus,  $\log f_{O_2}$  in the cuprian manganoan phlogopite-bearing thin layers is estimated to be  $-6.5 \pm 2$  at  $\sim 550$  °C by the thermodynamic data of Helgeson et al. (1978) and Robie et al. (1978) for the  $Cu_2O + CuO$  and  $Mn_3O_4 + Mn_2O_3$  buffers.

The chemical compositions of ferromagnesian minerals in the same thin section with the same mineral assemblage vary from grain to grain. This chemical variation

is most likely due to the limited mobility (<0.5 mm) of constituents that are incorporated in the ferromagnesian minerals during metamorphism. The thin layer of siliceous schists lacking sulfide minerals is embedded within dominant basic schists, which sometimes contain small amounts of sulfide minerals such as chalcopyrite and pyrrhotite. The absence of sulfide minerals in the thin layer and the occurrence of Cu as a constituent of phlogopite, aegirine augite, and tirodite in some siliceous schists indicate that differences in  $f_{S_2}$  persisted during metamorphism, probably as a result of limited mobility of S (e.g., Tracy and Robinson, 1988).

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