Experimental studies on the system phlogopite–manganese phlogopite at 1, 10 and 20 kbar and 750°C in presence of excess water under NNO buffer conditions

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High pressure and temperature experiments have been done in the $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (phlogopite; Ph)– $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (manganese phlogopite; MnPh) system under 1, 10, and 20 kbar at 750°C under NNO buffer conditions. The phases coexisting with phlogopite at 1 kbar include leucite, olivine, pyroxenoid, and manganese oxide. At 10 kbar, the equilibrium phases include phlogopite, olivine, manganese oxide, pyroxenoid, leucite and melt. At 20 kbar, they are phlogopite, olivine, pyroxenoid, manganese oxide and melt. The extent of solid solution of manganese phlogopite systematically increases with the increase of pressure and extent of solid solution being 17, 37, and 43 mol.% at 1, 10 and 20 kbar respectively.

Keywords: Mn-phlogopite, High pressure experiment, Solid solution

I. Introduction

Mn-bearing micas may provide important information on the P, T and f_{O_2} conditions of formation of Mn-rich metasedimentary rocks. The analyses of some tri-octahedral mica show a few thousandth to a few hundredth atoms of Mn per six octahedral sites (Deer *et al.*, 1967). This figure, however, does not correspond to saturation level, as phlogopite from Mn-rich assemblages contain much more Mn (Bailey, 1984). Phlogopite with considerable amounts of MnO (up to 7%) has been reported from viridine-bearing hornfels (Abraham and Schreyer, 1975; Smith and Albee 1967). Phen-gite, dioctahedral mica, containing up to 6.7% MnO (alurgite) has also been reported (Abraham and Schreyer 1975). Occurrence of these Mn-rich micas represent high abundance of Mn in bulk composition such that an intrinsic Mn-

bearing phase (piemontite or viridine) is present.

In a piemontite-bearing rock phlogopite containing exceptionally high MnO (17 wt.%) is reported (Abraham and Schreyer 1976), whereas phlogopite with 5% MnO has been recorded from a piemontite- and braunite-bearing rock (Brown *et al.*, 1978). Mn-phlogopite (Schaller 1930) have been reported to occur in association with rhodonite and also as inclusion within the garnets and pyroxenoids in gondites of Sausar group of rocks in India (Kilpady and Dave 1954). They have reported 5.58 wt.% MnO in the manganophyllite from the Sitasongi mines. Manganophyllite from the same locality (Roy and Mitra, 1964) yielded 2.67% MnO and 1.18% Mn_2O_3 respectively.

Very few studies have been carried out to prove the manganese content of natural and synthetic phlogopite (Jacob, 1925; Abraham

and Schreyer, 1976; Brown *et al.*, 1978; Kato *et al.*, 1979; Toraya *et al.*, 1983; Guggenheim, 1984). According to Jacob (1925) a maximum of 20% Mn^{2+} can be incorporated into the phlogopite structure. Experimental studies related to solubility of Mn in the phlogopite structure are rather few. There have been attempts to synthesize a pure manganese phlogopite end member (Lindquist 1963, Hewitt and Wones 1975) under various temperatures and controlled oxygen fugacity conditions. Experiments (Hazen and Wones, 1972) have been carried out under hydrothermal condition at 725°C and 2 kbar ($P_{\text{H}_2\text{O}} = P_{\text{Total}}$) with a maximum duration of 336 hours. These runs were performed at 1 kbar (P_{CH_4}). Most run products consisted of an assemblage tephroite + kalsilite + leucite + $\text{Mn}(\text{OH})_2$ or Mn_2O_3 + sanidine. Two runs were performed under 1 and 2 kb ($P_{\text{H}_2\text{O}}$) at 603°C (Fron del and Ito 1966). Results show the formation of an assemblage containing $\text{Mn}(\text{OH})_2$ + manganophyllite. Tephroite is reported to be present as a major phase in all the mica-bearing runs, but they failed to synthesize a pure Mn-phlogopite end member due to crystallochemical limitations. Synthetic mica suggests that the distorted octahedral site of phlogopite may stabilize manganese in the trivalent state (Burns, 1970).

In order to learn more about the phase relations of the system phlogopite-Mn-phlogopite, nine starting materials were prepared. Systematic investigation of the system at various temperatures under 1, 10 and 20 kbar using Ni-NiO buffer, was carried out in presence of excess water, so that $P_{\text{H}_2\text{O}} = P_{\text{Total}}$.

II. Experimental Technique

Following chemicals were used for making the starting materials: MgO , Al_2O_3 , MnCO_3 and K_2CO_3 . Reagent grade MgO and Al_2O_3 were heated in a furnace for one hour at 1000°C to get rid of water present either as $\text{Mg}(\text{OH})_2$

or $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} \cdot \text{MnCO}_3$ and K_2CO_3 were dried in an oven. Pure quartz (SiO_2 : 99.98 wt.%), collected from Matheran, Maharashtra was used as a source of silica. These chemicals were then weighed in a micro-balance in appropriate proportions to prepare a starting material of desired composition. Nine starting materials of following compositions were prepared:

$\text{Ph}_{90}(\text{MnPh})_{10}$, $\text{Ph}_{80}(\text{MnPh})_{20}$, $\text{Ph}_{70}(\text{MnPh})_{30}$, $\text{Ph}_{60}(\text{MnPh})_{40}$, $\text{Ph}_{50}(\text{MnPh})_{50}$, $\text{Ph}_{40}(\text{MnPh})_{60}$, $\text{Ph}_{30}(\text{MnPh})_{70}$, $\text{Ph}_{20}(\text{MnPh})_{80}$, and $(\text{MnPh})_{100}$.

The chemicals and quartz were mixed in an agate mortar with acetone. The mixture was dried in an oven so that any acetone present could be evaporated. A portion of the dried composition was then placed in a tubular platinum foil, which in turn was placed in a graphite capsule, the open end of which was also tightly fitted with a graphite cover. A whole was punctured in the cover so that unwanted volatile could escape. Whole assembly was then placed in a talc crucible and was heated in blue flame for two hours to drive out CO_2 . The composition was then crushed to powder in an agate mortar, and used for hydrothermal or high pressure runs.

Experiments at 10 and 20 kbar were conducted at the Department of Earth and Planetary Science, University of Allahabad, with a solid media piston cylinder apparatus (Kennedy type), supplied and manufactured by Toshiba Tungalay Company, Japan. Calibration of pressure and temperature of the equipment has made with respect to quartz-coesite transformation (Bohlen and Boettcher, 1982). Runs at 1 kbar and 750°C (in presence of excess water) were conducted in externally heated could seal pressure vessels. Double capsule method with buffer materials (Ni-NiO) in the outer capsule and the mixture in the inner capsule was employed for the present investigation.

The phases were identified with the help of

a petrographic microscope, a X-ray diffractometer (XRD) and an electron microprobe. Mineral analyses were made on an automated energy-dispersive electron microprobe of JEOL JSM-5300 and LINK QX2000J system (operating condition 15 kV and 0.15 nA) at Geological Institute, Yokohama National University, Japan. Some of the analyses were reproduced using a wave dispersive electron microprobe (JEOL JXA-8800M superprobe, operating condition 15 kV and 13 nA) at National Institute of Polar Research, Japan. Duplication of the analyses on the same sample yield comparable results at both institutes.

III. Phases

The phases obtained are olivine, K-feldspar, pyroxenoid (solid solution of MgSiO_3 and MnSiO_3), leucite, phlogopite and Mn oxide. Olivine is a solid solution of Mg_2SiO_4 and Mn_2SiO_4 . It occurs as euhedral crystal with domal top. Electron microprobe analyses show that, with the increase of Mn-Ph content in the starting composition, olivine becomes richer in tephroite. K-feldspar occurs as needles or rectangular plates with low birefringence. Electron microprobe analyses show that it is pure in composition. Manganese silicate appears as prismatic crystals with inclined extinction ($Z/C=33-44^\circ$). Indices of refraction measurement show that it has $N_\gamma=1.674\pm0.002$, $N_\alpha=1.665\pm0.002$. Judging from its optical properties and XRD data, it appears to have a structure similar to that of bustamite. Electron microprobe analyses show that it contains variable amounts of MgSiO_3 in solid solution. It was identified by its higher refractive indices and inclined extinction. Manganese oxides occur as opaque mineral; XRD data suggest that it is Mn_3O_4 in composition.

Leucite usually occurs as perfect euhedral isotropic crystal with eight sided out line, but sometimes it is rounded. Schairer (1948)

observed complete solid solution between leucite and a compound $\text{K}_2\text{O}\cdot\text{MgO}\cdot5\text{SiO}_2$. The structural formulae of leucite suggest the presence of $\text{K}_2\text{O}\cdot\text{MnO}\cdot5\text{SiO}_2$ molecule in leucite in minor amounts. The maximum amount of MnO incorporated in leucite structure is 0.04 mol.%.

Phlogopite occurs as euhedral grains with hexagonal outline. X-ray diffraction patterns of phlogopite suggest that they are 1 M or 3 T polytype, 2 M type is not encountered. Mica is also identified by its peaks at 8.8° , 26.6° and 34.2° $\text{CuK}\alpha 2\theta$. All these three peaks are found to shift, when substitution of Mn for Mg occurred. Electron microprobe analyses of mica shows that it is a solid solution between $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ and $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. Detailed discussion on the extent of solid solution of $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ in phlogopite will be discussed later.

IV. Results and Discussions

1. Mineralogical Significance at 1 kbar

Experimental results related to 1 kbar are summarized in Table 1. The assemblage phlogopite, olivine, leucite, $(\text{Mg}, \text{Mn})\text{SiO}_3$ and Mn_3O_4 can be expressed by the following reaction:

It was observed that reflection (100) of phlogopite solid solution crystallized at 750°C is sensitive to the increase of MnPh content (Fig. 1a). Variation in the position of 2θ (100) as a function of composition shows a change in the slope of the curve around 25 mol.% MnPh, suggesting that phlogopite can incorporate about 25 mol.% $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ in solid solution. Refractive index measurement [$(N_\beta = N_\gamma)$ ver-

Table 1. The experimental results of the system Phlogopite-Mn-Phlogopite at 750°C and 1, 10, and 20 kbar under NNO buffer condition

Starting Composition	Result
At 1 kbar	
Ph ₉₀ MnPh ₁₀	Ph+tr Ol
Ph ₈₀ MnPh ₂₀	Ph+tr Lc+ tr Ol
Ph ₇₀ MnPh ₃₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₆₀ MnPh ₄₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₅₀ MnPh ₅₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₄₀ MnPh ₆₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₃₀ MnPh ₇₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₂₀ MnPh ₈₀	Ph+Lc+Ol+Ms+Mn-Oxide
Ph ₀₀ MnPh ₁₀₀	Ol+Ms+Lc+Gl+Mn-Oxide
At 10 kbar	
Ph ₉₀ MnPh ₁₀	Ph
Ph ₈₀ MnPh ₂₀	Ph+tr Ol
Ph ₅₀ MnPh ₅₀	Ph+ tr Ol + tr Ms
Ph ₃₀ MnPh ₇₀	Ph+Ol+Ms+Gl+Mn-Oxide
Ph ₂₀ MnPh ₈₀	Ph+Ol+Gl+Ms+Mn-Oxide
Ph ₀₀ MnPh ₁₀₀	Ph+Ms+Lc+Gl+Mn-Oxide
At 20 kbar	
Ph ₉₀ MnPh ₁₀	Ph+tr Ol
Ph ₈₀ MnPh ₂₀	Ph+tr Ol
Ph ₇₀ MnPh ₃₀	Ph+tr Ol
Ph ₄₀ MnPh ₆₀	Ph+Ol+Gl+Ms+Mn-Oxide
Ph ₃₀ MnPh ₇₀	Ph+Ol+Gl+Ms+Mn-Oxide

Abbreviations: Ph, phlogopite; Ol, olivine; Lc, leucite; Ms, pyroxinoid; Gl, glass; tr, trace amount.

sus a Mn-phlogopite] of phlogopite_{ss} crystallizing in the system $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ - $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (Fig. 1b) also confirms that phlogopite can incorporate up to 20 mol.% $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ in solid solution. Same inference can be drawn from Fig. 1c, in which $N\alpha$ of phlogopite solid solutions is plotted against Mn-phlogopite content in the starting material. Microprobe analyses of these synthetic phlogopite_{ss} was determined (Table 2). When content of $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ is plotted

Fig. 1. (a) Variation of 2θ ($\text{CuK}\alpha$) value for the reflection (100) of Mn-Phlogopite-phlogopite solid solution (synthesized at 10 kbar and 750°C) as a function of composition. (b) Variation in the refractive index ($N\beta=N\gamma$) of mica (crystallized at 1 kbar and 750°C) as a function of composition. (c) Variation in the refractive index ($N\alpha$) of mica (crystallized at 1 kbar and 750°C) as a function of composition.

against the compositions of different starting materials, it is noted that phlogopite can incorporate 17 mol.% $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ in solid solution under 1 kbar at 750°C (Fig. 2a).

Measurement of refractive indices on synthetic phlogopite-Mn-phlogopite solid solution and its composition agrees well with those of Mn-rich natural micas (Kilpady and Dave 1954, Roy and Mitra 1964, Eugster and Wones 1962). The refractive indices of manganophyllite from Sitasong mines range between $N\gamma=1.600$ to 1.612. This indicates that from the Sitasong mine, Maharashtra, might have equilibrated at low pressure close to 1 kbar $P_{(\text{H}_2\text{O})}$. Mica

Table 2. Microprobe analyses of phlogopite

P (kbar)	1	1	1	10	10	10	10	20	20	20	20
T (°C)	750	750	750	750	750	750	750	750	750	750	750
Ph-MnPh*	90-10	80-20	30-70	90-10	80-20	50-50	30-70	90-10	80-20	40-60	30-70
SiO ₂	42.30	44.27	41.21	42.27	41.72	40.01	39.92	42.25	41.56	39.92	39.46
Al ₂ O ₃	12.01	10.62	12.32	11.95	11.75	11.38	11.29	11.91	11.65	11.29	11.16
MnO	4.10	7.81	8.34	5.02	8.41	16.65	17.55	5.04	8.88	17.55	20.06
MgO	26.21	23.39	23.20	25.20	23.16	17.31	16.80	25.54	22.59	16.80	15.07
K ₂ O	11.09	9.90	10.78	11.05	10.82	10.22	10.45	11.04	10.76	10.44	10.31
Total	95.61	95.99	95.76	95.79	95.86	95.57	96.01	95.78	95.44	96.00	96.06
O=22											
Si	5.976	6.269	5.927	6.008	5.999	5.999	5.993	5.989	6.015	5.993	5.994
Al	2.000	1.773	2.088	2.002	1.991	2.011	1.998	1.990	1.987	1.998	1.998
Mn	0.491	0.937	1.016	0.604	1.024	2.114	2.232	0.605	1.089	2.232	2.581
Mg	5.558	4.971	5.008	5.375	4.998	3.895	3.785	5.434	4.907	3.785	3.435
K	1.999	1.788	1.978	2.003	1.985	1.955	2.001	1.996	1.987	1.999	1.998
Total	16.023	15.738	16.017	15.993	15.997	15.973	16.009	16.014	15.984	16.007	16.006
Mn/MnMg	0.08	0.16	0.17	0.10	0.17	0.35	0.37	0.10	0.18	0.37	0.43

*Starting composition

containing 8.1% MnO (19% Mn-Ph molecule) has been reported by Dal Piaz *et al.*, (1979) from piemontite-bearing mica schist occurring in Valsesia-Valtornach arc (Italian western Alps). Mica containing 6% MnO (14.35% MnPh) has been reported from viridine-bearing hornfels by Smith and Albee (1967) from San Gorgonio Pass, California. Phlogopite containing 6.7% MnO has been reported from viridine hornfels from Damstadt (Germany) by Abraham and Schreyer (1975).

Bowen *et al.* (1978) described phlogopite containing 5% MnO (11.96% MnPh) from manganese-rich rocks of St. Marcel, Piedmont Italy. Mica containing 5.58% MnO occurs in Sitaswami mines (Kilpady and Dave, 1954). Manganophyllite from the same locality however is reported to contain 2.67% MnO (Roy and Mitra, 1964). The present study suggests that all these micas have crystallized at low pressure similar to that of green schist facies.

Table 3 demonstrates that olivine crystallizing in equilibrium with Mn-bearing phlogopite and pyroxenoids (Mg, Mn)SiO₃ under NNO buffer condition at 1 kbar has a complete solid solution relation between

Mg₂SiO₄ and Mn₂SiO₄. While those crystallizing from starting materials having lower KMn₃AlSi₃O₁₀(OH)₃ content are enriched in forsterite molecule, those starting materials having higher amount of this molecule are richer in tephroite as expected. It is noted that pyroxenoids crystallizing from the compositions Ph₂₀MnPh₈₀ at 1 kbar and 750°C under NNO buffer conditions contains relatively high MnO (27.64 wt.%) (Table 4). As only 17 mol.% of KMn₃AlSi₃O₁₀(OH)₂ is incorporated into phlogopite_{ss}, the excess MnO is also incorporated by olivine as tephroite molecule (Table 3).

Scharirer (1948) established complete solid solution relationship between leucite and K₂O • MgO • 5SiO₂ molecule; however microprobe analyses demonstrate the presence of minor amount of MnO possibly as K₂O • MnO • 5SiO₂ in solid solution with no Mg entering into its structure (Table 3). The maximum amount of MnO that was found to be incorporated by leucite as K₂O • MnO • 5SiO₂ molecule is about 1.1 wt.% at 1 kbar and 750°C under NNO buffer condition.

2. Mineralogical Significance at 10 kbar

The phase assemblages obtained in the join

Fig. 2. (a) $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ content (mole%) of mica versus MnPh content in the starting materials crystallized at 750°C and 1 kbar. (b) $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ content (mole%) of mica versus MnPh content in the starting materials crystallized at 750°C and 10 kbar. (c) $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ content (mole%) of mica versus MnPh content in the starting materials crystallized at 750°C and 20 kbar.

Ph-MnPh under 10 kbar at 750°C is phlogopite(ss)+olivine(ss)+(Mn, Mg) SiO_3 + Mn_3O_4 and liquid. Microprobe analyses of phlogopite(ss) are given in Table 2. In Fig. 2b, the content of $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ as a function of the starting materials (with progressive increase of Mn content) is plotted. It is observed that at 10 kbar about 17.55 wt.% MnO [37 mol.% $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] can be incorporated in the phlogopite structure. Yoder and

Kushiro (1969) studied the stability of phlogopite up to a pressure of 35 kbar. They observed that at higher pressure and higher temperature, phlogopite melts incongruently to forsterite+liquid. The mass balance equation suggests that the liquid present along with phlogopite_{ss} evidently is enriched in potassium silicate. At low pressure breakdown of phlogopite to produce, leucite+kalsilite+forsterite has been studied by Yoder and Eugster (1954). As discussed in the proceeding section, leucite+olivine are accompanying phases at low pressure runs at 1 kb. In the system phlogopite-Mn-phlogopite, mica (containing up to 37 wt.% $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) is equilibrium with (Mg, Mn) SiO_4 and alkali alumino silicate melt. Under NNO buffer condition oxidation of Mn_2SiO_4 yields MnSiO_3 + Mn_3O_4 . Note the reaction :

At high pressure and low temperature in the subsolidus region, K-feldspar and Mn_3O_4 are equilibrium phases along with phlogopite_{ss}.

It may be observed that the Mn_2SiO_4 content of olivine is about 50, 77 and 81 mol.% for those crystallizing from compositions $\text{Ph}_{50}\text{MnPh}_{50}$, $\text{Ph}_{30}\text{MnPh}_{70}$ and $\text{Ph}_{20}\text{MnPh}_{80}$, respectively (Table 3). K-feldspar is almost pure and does not contain detectable amounts of MnO (Table 4).

3. Mineralogical Significance at 20 kbar

Experimental runs at 750°C and 20 kbar were conducted on five compositions ($\text{Fo}_{90}\text{MnPh}_{10}$, $\text{Fo}_{80}\text{MnPh}_{20}$, $\text{Fo}_{70}\text{MnPh}_{30}$, $\text{Fo}_{40}\text{MnPh}_{60}$ and $\text{Fo}_{30}\text{MnPh}_{70}$). In all of the run at 20 kbar, Mn-bearing phlogopite coexists with (Mg, Mn) SiO_3 , olivine_{ss}, Mn_3O_4 , and melt. The $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ content of phlogopite_{ss} equilibrated at 20 kbar and 750°C have been plotted as a function of Mn-phlogopite (Fig. 2c). It may be observed from Fig. 2c that

Table 3. Microprobe analyses of olivine and leucite

	olivine						leucite	
P (kbar)	1	1	1	10	10	10	1	1
T (°C)	750	750	750	750	750	750	750	750
Ph-MnPh*	90-70	20-80	60-40	50-50	30-70	20-80	30-70	60-40
SiO ₂	30.99	32.94	31.98	36.92	30.55	32.08	55.02	55.57
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	22.64	22.94
MnO	64.43	60.23	60.20	41.11	58.24	59.35	1.11	0.82
MgO	4.57	6.81	8.53	23.85	9.73	8.16	-	-
K ₂ O	-	-	-	-	-	-	20.35	21.00
Total	99.99	99.98	100.71	101.88	97.52	99.60	99.12	100.32
O=4							O=6	
Si	1.005	1.037	1.002	1.024	0.978	1.014	2.013	2.011
Al	0.000	0.000	0.000	0.000	0.000	0.000	0.976	0.979
Mn	1.769	1.606	1.598	0.966	1.579	1.588	0.034	0.025
Mg	0.221	0.320	0.398	0.986	0.464	0.384	-	-
K	-	-	-	-	-	-	0.950	0.070
Total	2.995	2.963	2.998	2.976	3.022	2.986	3.974	3.984

*Starting composition

Table 4. Microprobe analyses of (Mg, Mn)SiO₃, K-feldspar, and glass

	(Mg,Mn)SiO ₃		K-feldspar		glass	
P (kbar)	1	10	10	10	10	10
T (°C)	750	750	750	750	750	750
Ph-MnPh*	20-80	0-100	20-80	00-100	30-70	20-80
SiO ₂	53.84	49.43	65.20	63.41	51.05	56.21
Al ₂ O ₃	-	-	18.95	19.66	4.65	2.32
MnO	27.64	51.90	-	-	8.31	15.93
MgO	18.50	-	-	-	15.87	3.05
K ₂ O	-	-	17.24	16.95	15.07	21.01
Total	99.98	101.33	101.39	100.02	94.95	98.52
O=3			O=8		O=10	
Si	1.018	1.038	2.982	2.943	3.390	3.799
Al	-	-	1.022	1.075	0.364	0.185
Mn	0.443	0.923	-	-	0.467	0.912
Mg	0.521	-	-	-	1.571	0.307
K	-	-	1.006	1.003	1.276	1.811
Total	1.982	1.961	5.010	5.021	7.068	7.014

*Starting composition

at 20 kbar under NNO-buffer condition the maximum amount of $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ that can be incorporated by phlogopite under these physico-chemical condition is 43 mol.%.

Bailey (1984) tabulated the structural formulae of Mn-bearing phlogopites (both natural and synthetic). Some of the manganophyllite (Kato *et al.*, 1979, Guggenheim and Kato 1984), from Iwate, Japan have 8.67 wt.% and 17.06 wt.% MnO, respectively. A phlogopite from talc and phengite-bearing assemblage in piedmontite-bearing schist from Brezovica Serbia, Yugoslavia contains 17 wt.% MnO (about 37

mol.% MnPh).

The present study indicates that the maximum amount of manganese oxide entering into the structure of phlogopite is 20 wt.% at 750°C and 20 kbar, which agrees with the composition of the natural phlogopites from Japan and Yugoslavia. Such high content of MnO in phlogopite is expected to have formed at pressure higher than 10 kb. Thus, experimental studies under 1, 10 and 20 kbar and 750°C show that the extent of solid solution of manganese phlogopite systematically increases with the increase of pressure and extent of solid solution being 17, 37 and 43 mol.% at 1, 10 and 20 kbar respectively.

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水の存在下, 1, 10 および 20 kbar, 750°C における金雲母—マンガン金雲母系の安定関係

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金雲母 ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$; Ph)-マンガン金雲母 ($\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$; MnPh) 系の高圧・高温実験を 1, 10, 20 kbar の圧力範囲で行った。1 kbar において, 金雲母は leucite, olivine, pyroxenoid, そして manganese oxide と平衡に共存した。10 kbar では, phlogopite, olivine, manganese oxide, pyroxenoid, leucite, melt の組合せが, 20 kbar では phlogopite, olivine, pyroxenoid, manganese oxide, melt の共存が確認された。金雲母中へのマンガン金雲母の固溶範囲は, 圧力増大により増加し, 1, 10, 20 kbar の圧力下でそれぞれ, 17, 37, 43 mol.% であった。