4674

Nat. Acad. Sci. Letters, Vol. 16, No. 1, 1993

Experimental studies on the system Phlogopite-Mn-Phlogopite at 1 and 10 kbars and variable temperatures in presence of excess water under NNO buffer conditions

(manganese solubility/phlogopite/NNO buffer)

RUCHIRA KAR AND ALOK K. GUPTA

Department of Earth and Planetary Sciences, University of Allahabad, Allahabad-211002, India.

Received 15-11-1992

ABSTRACT Experimental studies on 8 compositions in the Phlogopite (Ph) Mn-Phlogopite (MnPh) system at 800 (1 kb) and 750°C (10 kb) under NNO buffer conditions show that phlogopite can incorporate up to about 50 wt% MnPh in solid solution. Pure Mn-phlogopite is not stable at 1 kb, but could be synthesized at 10 kb. Mn-phlogopite can incorporate up to 30 wt% Ph in solid solution.

Micas are quite extensive in their occurrence in igneous, metamorphic and sedimentary rocks. It is considered as one of the most important rock-forming minerals[1] with a wide range of chemical composition. In the metapelites, micas are involved in most of the important isograd reactions, especially biotite isograd. Mn-bearing micas provide important constraints on the P, T,f_{O_2} grid of Mn-rich metasedimentary rock. Not only tri-octahedral but also di-octahedral micas contain small amount of Mn (e.g. 0.01 atom per-4-octahedral sites). In a few typical compositions such as piemontite-bearing schist, the co- existing mica can contain high amount[2] of Mn (8.1%). Phlogopite with 7% Mn has also been reported earlier[3]. Mica containing 6% MnO has also been reported from some viridine-bearing hornfels[4]. Phengite containing up to 6.7% MnO (alurgite) has also been reported from nature[3]. Occurrence of such Mn-rich micas represent uncommon bulk composition such that an intrinsic Mn-bearing phase (piemontite or viridine) is present.

The tri-octahedral mica analysis show a few thousand to a few hundreds atom of Mn per six octahedral sites. However, these amounts are almost surely not at saturation levels, as phlogopite from Mn-rich assemblages[5] contain much more Mn. Very few studies have been carried out to probe the manganese content of natural and synthetic phlogopite[6-11]. A maximum of 20% Mn^{2+} can be incorporated into the phlogopite structure[6]. In a piemontite- bearing rock, phlogopite containing 17% MnO is reported[7], whereas phlogopite with 5% MnO has been recorded from a piemontite and braunite-bearing rock[8]. Mn-phlogopite[12] have been reported to occur in association with rhodonite and also as inclusion within the garnets and pyroxenoids in the gondite of Sausar group of rocks in India[13]. They have reported 5.58% MnO in the manganophyllite from the Sitasaongi mines. Manganophyllite from the same locality[14] yielded 2.67% MnO and 1.18% Mn_2O_3.

Experimental studies are almost non-cxistent to show the maximum solubility of manganese molecule in the phlogopite structure. However, there have been attempts to synthesize a pure manganese phlogopite end member[15,16] under various temperatures and controlled oxygen fugacity conditions. Experiments[17] have been carried out under hydrothermal condition at 725°C and 2 kb ($P_{H_2O} = P_{total}$) with a maximum duration of 336 hours. Three runs were performed at 1 kb (P_{CH_4}). Most run products consisted of an assemblage comprising tephroite + kalsilite + leucite or $Mn(OH)_2$/-Mn_2O_3 + sanidine. Two runs were performed under 1 and 2 kb (P_{H_2O}) at 603°C. Results show the formation of an assemblage containing $Mn(OH)_2$ + manganophyllite. Tephroite is reported to be present as a major phase in all the mica-bearing runs[18], but they failed to synthesize a pure Mn-phlogopite end member due to crystallochemical limitations of mica structure[17]. Absorption spectra of synthetic mica suggests that the distorted octahedral site of phlogopite may stabilize manganese in the trivalent state[19].

In order to learn more about the phase relations of the system phlogopite-Mn-phlogopite, eight starting materials were prepared. Systematic investigation of the system at various temperature under 1 and 10 kbar using Ni-NiO buffer, was carried out in presence of excess water, so that $P_{H_2O} = P_{total}$.

Following chemicals were used for making the starting material. MgO, Al_2O_3, SiO_2, $MnCO_3$ 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 $Mg(OH)_2$ or $Al_2O_3 . nH_2O$ as impurities. $MnCO_3$ and K_2CO_3 were dried in an oven. Pure quartz 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. Eight starting materials of following compositions were prepared: Ph_{80}-$MnPh_{20}$, $Ph_{70}MnPh_{30}$, Ph_{60} $MnPh_{40}$, Ph_{50}-$MnPh_{50}$, Ph_{40}-$MnPh_{60}$, Ph_{30}-$MnPh_{70}$, Ph_{20}-$MnPh_{80}$, and Ph_{00}-$MnPh_{100}$. The oxide mixtures were mixed in an agate mortar with acetone. The mixture was left open for a few minutes till all the acetone got evaporated. A portion of the dried composition was then placed in a tube shaped platinum foil, which in turn was placed in the graphite capsule. The whole assembly was then placed in a talc crucible and was heated in blue flame for two hours to drive out CO_2. After the crucible cooled down, the composition was taken out from the platinum foil. The starting composition showed a change in colour. The composition was then crushed to powder form in an agate mortar, which was finally transferred in a vile ready for hydrothermal or high pressure runs. Eight experimental runs were performed at one kbar and 800°C in hydrothermal apparatus while five experimental runs were performed at 10 kbar and 750°C in piston cylinder apparatus. Double capsule method[20] with buffer materials (Ni-NiO) in the outer capsule and the mixture in the inner capsule was employed for the present investigation. Excess water was always placed in the capsule so that $P_{H_2O} = P_{total}$. The outer capsule was always welded shut.

Experimental results are summarized in Tables (1 & 2). The phases present, were confirmed by a microscope and a X-ray diffractometer. The assemblages 1: (Ph + Lc

Table 1 - The experimental data of the system Phlogopite-Mn- Phlogopite at 1 kbar under NNO buffer condition.

Run No.	Composition	Temp. (°C)	Run Products.
1.	$Ph_{80}\,MnPh_{20}$	800	Ph + Lc + F + Ks + Ms + Oxide
2.	$Ph_{70}\,MnPh_{30}$	800	Ph + Lc + F + Ks + Ms + Oxide
3.	$Ph_{60}\,MnPh_{40}$	800	Ph + Lc + F + Ks + Ms + Oxide
4.	$Ph_{50}\,MnPh_{50}$	800	Ph + Lc + F + Ks + Ms + Oxide
5.	$Ph_{40}\,MnPh_{60}$	800	Ph + Lc + F + Ks + Ms + Oxide
6.	$Ph_{30}\,MnPh_{70}$	800	Ph + Lc + F + Ks + Ms + Oxide
7.	$Ph_{20}\,MnPh_{80}$	800	Ph + Lc + F + Ks + Ms + Oxide
8.	$Ph_{00}\,MnPh_{100}$	800	Gt + Ks + Ms + Gl + Oxide

Table 2 - The experimental data of the system Phlogopite-Mn- Phlogopite at 10 kbar under NNO buffer condition.

Run No.	Composition	Temp. (°C)	Run Products
1.	$Ph_{80}\,MnPh_{20}$	750	Ph + F + Gl + Ms + Oxide
2.	$Ph_{50}\,MnPh_{50}$	750	Ph + F + Ms + Ks + Gt + Oxide
3.	$Ph_{30}\,MnPh_{70}$	750	Ph + F + Ms + Gl + Gt + Oxide
4.	$Ph_{20}\,MnPh_{80}$	750	Ph + F + Gl + Ms + Gt + Oxide
5.	$Ph_{00}\,MnPh_{100}$	750	Ph + Ms + Gt + Lc + Gl + Oxide

Abbreviations : Ph - Phlogopite, Ks - Kalsilite, F - Olivine, Lc - Leucite, Ms - Manganese silicate, Gt - Garnet, Gl - Glass.

+ Ol + Ks) and 2: (Ph + Gt + Ks + $MnSiO_3$ + manganese oxide + L) can be expressed by the following reaction :

$K_2O.\,6MgO\,.\,Al_2O_3\,.\,6\,SiO_2\,.\,2H_2O$ +
(phlogopite)

$K_2O.\,6MnO\,.\,Al_2O_3\,.\,6\,SiO_2\,.\,2H_2O$
(Mn-phlogopite)

$\rightarrow 2\,KAlSi_2\,O_6 + 2\,KAlSiO_4$
(leucite) (kalsilite)

$+\,3\,Mn_2\,SiO_4\,.\,3\,Mg_2SiO_4 + 4H_2O$
(olivine)

Because of oxidation of $Mn_2\,SiO_4$ (note the reaction [$3Mn_2\,SiO_4 + \frac{1}{2}\,O_2 \rightarrow 3MnSiO_3 + Mn_3O_4$--(3)], formation of $MnSiO_3$ and Mn_3O_4 was encountered in both sets of assemblages. As the amount of oxide was very small, the exact identification of the oxide was not possible by X-ray. In this calculation, all phases have been considered to be pure. Whenever garnet was present, a liquid phase was encountered. In that case the break down products of $KMn_3\,AlSi_3O_{10}\,(OH)_2$ can be explained by the following reaction :

$2(K_2O.6MnO.Al_2O_3.6SiO_2.2H_2O) + \frac{1}{2}O_2$
(Mn-phlogopite)

$\rightarrow 2\,KAlSiO_4 + Mn_3\,Al_2\,Si_3O_{12} + 6\,MnSiO_3$
(kalsilite) (spessartine)

$+\,Mn_3O_4 + K_2O\,.\,SiO_2 + 4H_2O$
(liquid)

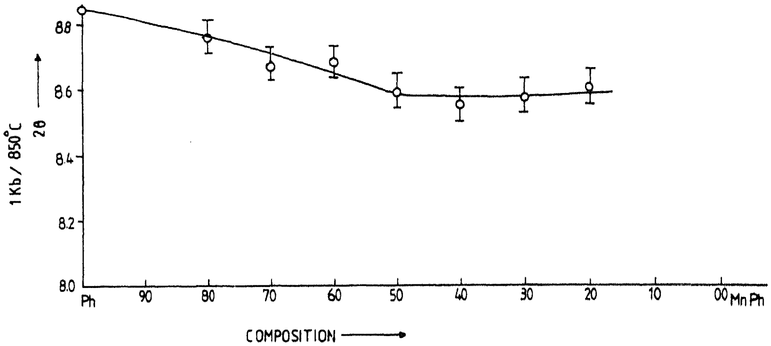

Fig. 1a - Variation of 2θ (CuKα) value for the reflection (100) of Phlogopite-Mn-Phlogopite solid solution (synthesized at 1 kbar and 800°C) as a function of composition.

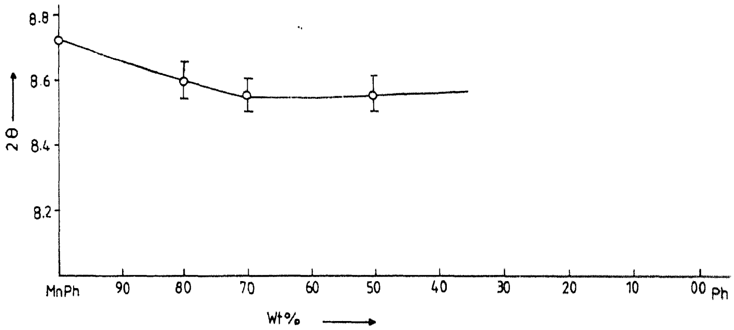

Fig. 1b - Variation of 2θ (CuKα) value for the reflection (100) of Mn-Phlogopite-Phlogopite solid solution (synthesized at 10 kbar and 750°C) as a function of composition.

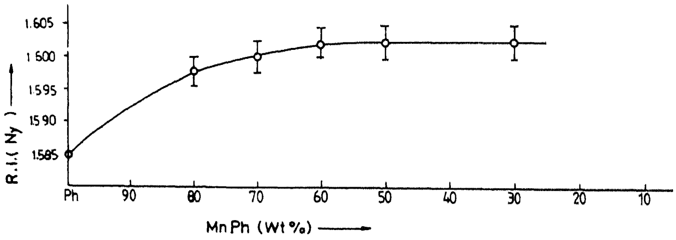

Fig. 2a - Variation in the refractive index ($N_\beta \cong N_\gamma$) of mica (crystallized at 1 kbar and 800°C) as a function of composition.

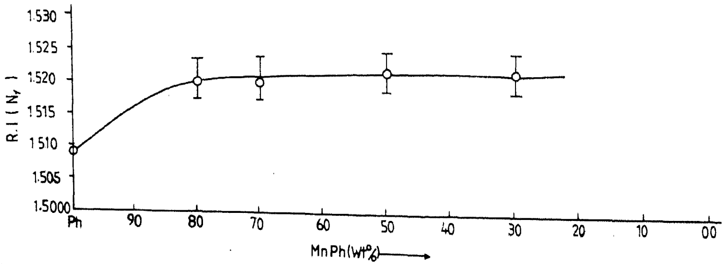

Fig. 2b - Variation in the refractive index (N_α) of mica (crystallized at 1 kbar and 800°C) as a function of composition.

The phases obtained in the join Ph-MnPh under 10 kbar isobaric section is

$$Ph + Ol + Ks + MnSiO_3 + Mn_3O_4 + L.$$

The exact position of the reflection-100 measured in terms of 2θ was plotted against composition. It can be observed from Fig.1(a) that between Ph_{100}-Ph_{50} $MnPh_{50}$, the variation in 2θ values is continuous with a sharp break near $Ph_{50}MnPh_{50}$, where a change in the gradient of the curve is noted. It is, therefore, concluded from this figure that phlogopite can incorporate 50 wt% manganese phlogopite in solid solution. It is also noted that at 1 kbar pure manganese phlogopite ($K_2O.6MnO.Al_2O_3.6SiO_2.H_2O$) is not stable, but it breaks down to Gt + Ks + $MnSiO_3$ + Mn_3O_4 + Gl.

Likewise, in case of runs at 10 kbar under NNO buffer condition, shows that phlogopite can incorporate 50 wt% of MnPh. It was observed that Mn-phlogopite is stable at 10 kbar and it can incorporate 30 wt% of phlogopite in solid solution (Fig.1(b)). An attempt was made to synthesize MnPh at 750°C and 6 kbar. Although the yield was very poor (confirmed by R.I. measurement), a rare amount of MnPh could be detected along with the same phases obtained with pure Mn-phlogopite run at 10 kbar and 750°C. X-ray diffraction pattern, however, failed to show its presence. Refractive indices measurements of mica ($N_\gamma = N_\beta$ and N_α) were made by using standard refractive index liquids (Cargille Laboratories U.S.A.) by liquid immersion method. Variation in the indices of refraction for the intermediate compositions is plotted in Figs. (2(a) & 2(b)); which show that N_γ for mica varies from 1.585 (pure phlogopite) to 1.602 ($Ph_{50}MnPh_{50}$); likewise, N_α varies from 1.508 (pure phlogopite) to 1.522 ($Ph_{50}MnPh_{50}$). Our measurement of refractive indices on synthetic phlogopite-Mn-phlogopite solid solution agrees very well with those of Mn-rich natural micas[13,14,21]. The refractive indices of manganophyllite from Sitasaongi mines range between N_γ = 1.60 to 1.612. This indicate that micas from the Sitasaongi mine, Maharashtra, might have equilibrated at pressure close to 1 Kb $P_{(H_2O)}$.

Bailey[5] tabulated the structural formulae of Mn-bearing phlogopites (both natural and synthetic). Some of the manganophyllite[9,22] from Iwate, Japan have their MnO content 8.67% and 17.06% respectively. The present study indicate that the maximum amount of manganese oxide entering into the structure of phlogopite is 20 wt%, which agrees with the composition of the natural phlogopites from Japan. Further experimental studies under high pressure is necessary to see whether the extent of solid solution of manganese phlogopite could increase with the increase of pressure.

One of the authors (A.K.G.) thanks the C.S.I.R., New Delhi for providing funds (Grant No. 24(179)/87-EMR II-May 87) for completing this study. The research associateship to the other author (R.K.) by the C.S.I.R., New Delhi is also gratefully acknowledged.

REFERENCES

1. Deer, W.A., Howie, R.A. & Zussman. J. (1967) *An Introduction to the Rock Forming Minerals*, ELBS Longman Group Ltd., New Delhi, p. 528.

2. Dal Piaz, G.V., Battistini, G.Di, Kienast, J.R. & Venturelli, G. (1979) *Mem. Sci. Geol. Gia Mom. degli Ist. Geol. Miner. dell Univ. di Padova* 32 : 24.

3. Abraham, K. & Schreyer, W. (1975) *Contrib. Mineral. Petrol.* **49** : 1.

4. Smith, D. & Albee, A.L. (1967) *Contrib. Mineral. Petrol.* **16** : 189.

5. Bailey, S.W. (1984) *Mineral. Soc. America* **13** : 13.

6. Jacob, J. (1925) *Z. Kristallogr.* **61** : 155.

7. Abraham, K. & Schreyer, W. (1976) *J. Petrol.* **17** : 421.

8. Brown, G., Essene, E.J. & Peacor, D.R. (1978) *Contrib. Mineral. Petrol.* **67** : 227.

9. Kato, I., Miura, Y., Yoshii, M. & Maeda, K. (1979) *Mineral. Jour. (Japan)* **9** : 392.

10. Guggenheim, S. (1984) *Mineral. Soc. America* **13** : 61.

11. Toraya, H. Marumo., F. & Hirao, M. (1983) *Mineral Jour. (Japan)* **11** : 222.

12. Schaller, W.T. (1930) *Amer. Mineral.* **15** : 566.

13. Kilpady, S.R. & Dave, A.S. (1954) *Current Science* **23** : 180.

14. Roy, B. & Mitra, F. N. (1964) *Proc. Nat. Inst. Sc. India* **30** **(3)** : 395.

15. Lindquist, B. (1963) *Geo. Foren. 1, Stockholm Forh.* **88** : 133.

16. Hewitt, D.A. & Wones, D. R. (1975) *Amer. Mineral.* **60** : 854.

17. Hazen, R.M. & Wones, D. R. (1975) *Amer. Mineral.* **57** : 103.

18. Frondel, C. & Ito, J. (1966) *Amer. Mineral.* **51** : 1107.

19. Burns, R.G. (1970) *Mineralogical Applications of Crystal Field Theory,* Cambridge University Press, Cambridge, England, p. 224.

20. Rao, K.V.R. (1955) *J. Geol. Min. Met. Soc. India* **27** : 131.

21. Eugster, H. P. & Wones, D. R. (1962) *J. Petrol.* **3** : 82.

22. Guggenheim, S. & Kato, T. (1984) *Mineral. Jour.* (Japan) **12** : 1.