

Petrology of Mg–Mn amphibole-bearing assemblages in manganese silicate rocks of the Sausar Group, India

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Abstract

Mg–Mn amphibole (tirodite), with or without pyroxmangite in the total absence of pyroxenes and high-calcic pyroxenoids, occurs in the Mn silicate rocks of the Sausar Group, India. The rocks were metamorphosed to amphibolite facies condition ($T \sim 650^\circ\text{C}$, $P \sim 6$ kbar). Tirodite–pyroxmangite pairs developed in both carbonate-free and rhodochrosite-bearing assemblages. Also tirodite coexists with either kutnahorite or manganoan calcite in the absence of pyroxmangite. Mineral reactions inferred from modal abundances and compositions of the phases indicate stabilization of the amphibole alone from a bivalent cation-bearing residual unbuffered X_{CO_2} system with $X_{\text{Mn}} < 0.3$. On the other hand, tirodite–pyroxmangite pairs appeared in unbuffered low to intermediate X_{CO_2} assemblages with $X_{\text{Mn}} > 0.35$. Pyroxenes and high-calcic pyroxenoids did not appear in the present situation, though they occur elsewhere in rocks with broadly similar contents of immobile components. Closely associated assemblages of diverse mineralogy suggest that the X_{Mn} and X_{CO_2} , rather than the physical conditions of metamorphism, are the decisive factors in promoting the observed phase assemblages.

KEYWORDS: magnesium, manganese, amphibole, tirodite, Sausar Group, India.

Introduction

Mg–Mn amphibole-bearing metamorphosed manganese silicate–carbonate rocks have been reported from Nsuta, Ghana (Jaffe *et al.*, 1961); Buritirama, Brazil (Peters *et al.*, 1977); Tatehira, Japan (Kobayashi, 1977) and Balmat, U.S.A. (Peterson *et al.*, 1984). Klein (1966) also described this phase from the Wabush iron-formation, Labrador. In all these deposits, except at Nsuta where data on accompanying minerals are lacking, Mg–Mn amphibole is associated with carbonate and pyroxene (Opx/Cpx) with or without rhodonite/pyroxmangite. The stability of Mg–Mn amphiboles with $X_{\text{Mn}} [= \text{Mn}/(\text{Mn} + \text{Mg})] < 0.3$ was investigated by Maresch and Czank (1983) and Huebner (1986). The effects of additional cations (such as Ca) and the composition of the fluid phase on the stability of Mn–Mg silicates and carbonates were studied by Abrecht and Peters (1980) and Winter *et al.* (1981). Brown *et al.* (1980) and Peterson *et al.* (1984) discussed the phase relations

between anhydrous members within the RSiO_3 tetrahedron ($R = \text{Mn–Mg–Ca–Fe}$). Based on field and experimental data, Huebner (1986) enumerated the possible phase relations between Mn–Mg silicates at 600°C and 4.5 kbar.

Despite the above studies, phase compatibilities of Mn silicates involving Mn amphiboles are still not clearly understood. This is obviously due to inadequate petrographic characterization of the rocks, incomplete chemical data of the coexisting phases, and difficulty in calculating X_{CO_2} for the metamorphic fluid. We present here petrographic and chemical data on Mg–Mn amphiboles and coexisting phases occurring in Mn silicate rocks of the Precambrian Sausar Group, India. This study is aimed at acquiring information on the formation of Mg–Mn amphiboles in diverse Mn silicate assemblages in relation to rock compositions, including mobile components, within amphibolite metamorphic facies.

Geological background

The Precambrian Sausar Group in central India hosts major metasedimentary manganese deposits

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mainly enclosed within the pelitic Mansar Formation (Roy, 1966). The Mn-rich formations consist of three rock types, viz. (i) Mn oxide ores, (ii) Mn silicate-oxide rock and (iii) Mn silicate-carbonate-oxide rock (Roy *et al.*, 1986). Both types of Mn silicate rock are thinly interbanded with the oxide ores and are finely interlaminated themselves. Assemblages with Mg-Mn amphiboles were recorded at Chikla (Bhandara District, Maharashtra), Tirodi (Balaghat District, Madhya Pradesh) and Mansar-Kandri (Nagpur District, Maharashtra). In all cases the enclosing pelites record the typical Barrovian type of metamorphism with development of almandine-rich garnet, staurolite, kyanite and sillimanite (Dasgupta *et al.*, 1984). Garnet-biotite thermometry in these pelites indicate culmination of metamorphism at $600 \pm 20^\circ\text{C}$ (Chikla), $650 \pm 25^\circ\text{C}$ (Tirodi) and $680 \pm 20^\circ\text{C}$ (Mansar-Kandri) at an estimated pressure of 6 kbar (Roy *et al.*, 1986). The mineralogy and mineral chemistry of the Mn oxide ores are given in Bhattacharya *et al.* (1984).

Petrography of the Mg-Mn amphibole-bearing assemblages

Petrographic descriptions of the diverse manganeseiferous assemblages in the Mn silicate rocks from the Sausar Group have been presented by Roy *et al.* (1986). Mg-Mn amphibole is present mainly in the silicate-carbonate rock and occurs only locally in the silicate-oxide rock. Representative mineral assemblages relevant to the present study are listed below.

- (i) Mg-Mn amphibole + spessartine-rich garnet + pyroxmangite + quartz + hematite (in the silicate-oxide rock)
- (ii) Mg-Mn amphibole + rhodochrosite + pyroxmangite + quartz + hematite (\pm garnet)
- (iii) Mg-Mn amphibole + kutnahorite + quartz + hematite (\pm garnet)
- (iv) Mg-Mn amphibole + calcite + quartz + hematite (\pm garnet).

The assemblages (ii) to (iv) are restricted to Mn silicate-carbonate rocks. Mg-Mn amphibole occurs as radiating needles in the Mn silicate rocks. It shows equilibrium textures with pyroxmangite and/or carbonates as well as with garnet. Quartz in assemblages (ii) to (iv) does not show any physical contact with the carbonates.

Characteristics of Mn silicates and related considerations

The amphibole is light yellow in colour with $Z \wedge C$ of $10-16^\circ$. The cell constants determined from powder diffraction data are $a 9.541 \pm 0.02$, b

18.129 ± 0.02 , $c 5.483 \pm 0.02 \text{ \AA}$, $\beta = 102.5^\circ$ (refined from 12 reflections). The chemical composition of the phase is given in Table 1. The structural content shows that Mn is greater than 2 (out of the total of 15 cations) and this corroborates the observation of Huebner (1986) that Mn can occupy sites other than $M(4)$ in Mn amphiboles. This amphibole, thus, corresponds to manganoan cummingtonite which has been equated to the varietal name tirodite by Leake (1978), though the tirodite from the type area (Tirodi, India) was earlier described as a manganoan alkali amphibole with the richterite (Dunn and Roy, 1938; Bilgrami, 1955), magnesiorichterite-magnesioriebeckite (Ghose *et al.*, 1974), and tremolite-richterite (Roy, 1974) composition. However, the IMA Commission adopted the name tirodite for manganoan cummingtonite and this nomenclature is followed henceforth.

Pyroxmangite in the studied assemblages was identified from optical ($2V \simeq 45^\circ$) and X-ray data ($a 6.72 \pm 0.01$, $b 7.606 \pm 0.02$, $c 17.45 \pm 0.02 \text{ \AA}$, $\alpha = 114.12^\circ$, $\beta = 82.4^\circ$, $\gamma = 93.6^\circ$), as well as chemical composition (Table 1). The composition of the garnets (Table 2) in the carbonitic assemblages show significant amounts of calderite and minor amounts of andradite and pyrope end members. Optical and chemical data (Table 1) indicate the presence of only one carbonate phase in each assemblage.

It is apparent from the compositions of the minerals in the different assemblages that they evolved in rocks which can be represented by a Mn-Mg-Ca-Fe-Al-Si-fluid system. The bulk chemical composition of the rocks corresponding to the given assemblages could not be determined because they occur as fine interbanded layers of contrasting composition, defying attempts at complete separation. The presence of appreciable hematite in the assemblages attests to an iron-rich bulk composition. At the same time, the non-appearance of magnetite indicates that the ambient f_{O_2} was above the HM buffer, thus restricting iron to the trivalent state. The available Al in the rock stabilized garnet which also accommodated trivalent iron as calderite and andradite components. Thus, the tirodite \pm pyroxmangite \pm carbonate + quartz assemblages evolved from the MnO-MgO-CaO-SiO₂-CO₂-H₂O system. The four types of assemblages are as follows:

- (i) Tirodite + pyroxmangite + quartz
- (ii) Tirodite + pyroxmangite + rhodochrosite + quartz
- (iii) Tirodite + kutnahorite + quartz
- (iv) Tirodite + calcite + quartz.

Modal abundances of these phases in each assemblage are given in Table 3.

Cation distribution patterns, probable mineral reactions and X_{CO_2} during metamorphism

The compositions of the coexisting tirodite and carbonates are shown in $X_{Ca}-X_{Mn}$ space in Fig. 1. Though the composition of tirodite varies little, that of the carbonates shows wide scatter. Ca is increasingly partitioned into carbonates at the expense of tirodite in assemblages (ii) to (iv). $K_{D_{Ca-Mn}}^{Ti-Carb} [(X_{Mn}/X_{Ca})^T/(X_{Mn}/X_{Ca})^C]$ varies from 0.26–1.33 in assemblage (ii), 9.6–14.4 in (iii) and 588–868 in (iv).

Table 2. Composition of garnets in assemblages (i), (ii) and (iii) determined by EPMA.

Assemblage	(i)	(ii)	(iii)
SiO ₂	36.24	35.88	35.78
TiO ₂	0.04	0.15	0.22
Al ₂ O ₃	19.58	14.34	12.59
Fe ₂ O ₃	1.05	9.79	11.24
MnO	41.80	36.67	38.45
MgO	0.17	0.74	0.54
CaO	0.28	3.22	1.74
Total	99.30	100.79	100.56
(O)	12.00	12.00	12.00
Si	3.011	2.989	3.021
Ti	0.002	0.01	0.014
Al	1.918	1.408	1.253
Fe ³⁺	0.066	0.614	0.714
Mn ²⁺	2.942	2.587	2.75
Mg	0.021	0.092	0.068
Ca	0.025	0.287	0.157
End-member components			
Spessartine	96.00	68.00	61.00
Andradite	0.4	9.0	5.3
Calderite	2.9	20.0	31.5
Pyrope	0.7	3.0	2.2

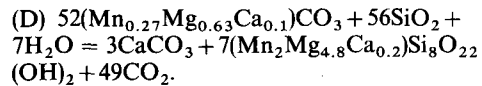
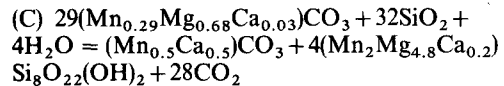
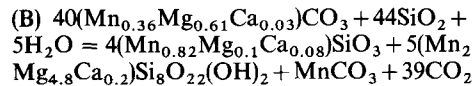
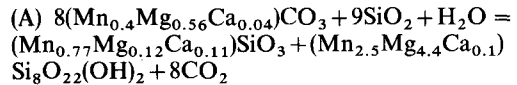
As it was impossible to determine the bulk composition of the rocks accurately, an evaluation of the probable influences of Mn:Mg:Ca ratios on the stability of the Mn silicates was attempted through inferred mineral reactions. The following reactions are based on assumed carbonate-silica precursors and the modal abundances and the actual chemical composition of the phases present.

Table 3. Modal abundance of the phases in the different assemblages.

Phase	Assemblage			
	(i)	(ii)	(iii)	(iv)
Tiroadite	43	40	55	50
Pyroxmangite	41	30	-	-
Carbonate	-	8	14	20
Others*	16	22	31	30

* Includes various combinations of hematite, quartz and garnet.

Cations present as dilute solutions were neglected while balancing the reactions



It is evident from the modal abundances of the phases present, such as spessartine-rich garnet and hematite (Table 3), that the original sediments were highly enriched in Mn and Fe. Such precursors could be Mn-rich carbonates and silica as indicated by the presence of similar assemblages in unmetamorphosed Mn-rich sedimentary deposits [cf. Usinsk deposit, U.S.S.R. Cambrian (Varentsov, 1964); Molango deposit, Mexico, Jurassic (Tavera and Alexandri, 1972); modern loch Fyne deposit, Scotland (Calvert and Price, 1970)]. The derived reactions, therefore, yield a good approximation for the Mn, Mg and Ca in the system available for the formation of bivalent cation-bearing Mn silicates and carbonates. The reactions show that tirodite could appear from varying $X_{Mn} [= Mn/(Mn + Mg + Ca)]$ in the system at the $P-T-X_{CO_2}$ metamorphic conditions studied. It is interesting (Table 1) that the Mg and Ca contents of tirodite did not vary significantly despite their variation in the system. In rocks with lower X_{Mn} (< 0.3), tirodite acted as a sink for the available Mg. This phase is also developed in rocks with higher X_{Mn} but in such cases too it maintains a near constant composition.

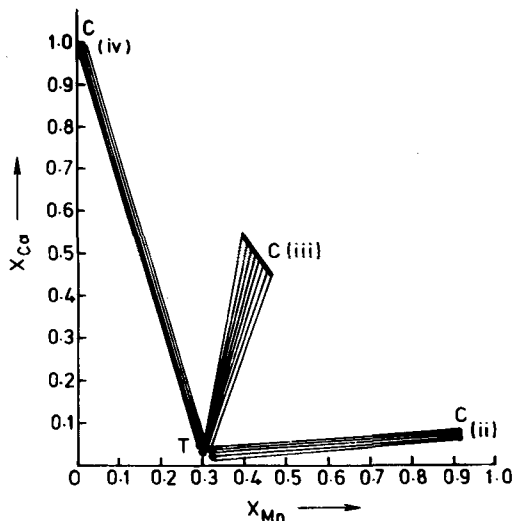


FIG. 1. Composition of the coexisting tirodite and carbonates in X_{Ca} - X_{Mn} space in assemblages (ii), (iii) and (iv).

Stabilization of pyroxmangite as an associated mineral required slightly higher X_{Mn} (> 0.3) in the rock. The appearance (reaction B) and non-appearance (reaction C) of pyroxmangite from identically low calcic bulk compositions indicates that either Ca at the available levels of concentration did not influence the stability of the phase or that it has an antipathetic relation with the stability of Ca-bearing carbonate.

The absence of approximate experimental data prevents the precise delineation of P , T and X_{CO_2} during the metamorphic reactions that could stabilize the studied assemblages. The diversity of

mineral assemblages in the spatially adjacent rocks indicates, however, that the physical conditions of metamorphism alone were not responsible for the observed phase relations. Disappearance of the carbonate phase from the reactant sides of the inferred mineral reactions suggests that these assemblages resulted from unbuffered X_{CO_2} reactions. The X_{CO_2} during such reactions can be qualitatively assessed on the basis of the experimental work of Peters (1971) and the calculations of Winter *et al.* (1981) on the stability of pyroxmangite. Pyroxmangite requires high X_{H_2O} (> 0.5) in the metamorphic fluid for its stable appearance in the amphibolite facies. This implies an influx of water during metamorphism to yield high X_{H_2O} inducing development of assemblages (i) and (ii) from precursors of carbonate-silica mixes. A similar model was conceived by Winter *et al.* (1981) to explain mineral paragenesis of the Bald Knob manganese deposit. Thus, the type (i) assemblage, with pyroxmangite in the absence of any carbonate, is evidently suggestive of a low X_{CO_2} situation and assemblage (ii) with rhodochrosite as an additional phase would represent an intermediate X_{CO_2} situation. Assemblages (iii) and (iv), without pyroxmangite and containing high Ca carbonate, represent high X_{CO_2} derivatives. This is shown in a schematic diagram (Fig. 2), where the compositions of the coexisting phases are plotted in CaO-MnO-MgO space (projected from H_2O , CO_2 and quartz). The tirodite-carbonate tie lines show a clockwise rotation with increasing X_{CO_2} and disappearance of pyroxmangite. The stability of pyroxmangite is thus influenced by both X_{Mn} and X_{CO_2} . This study thus shows that the development of different Mn silicate-bearing assemblages under identical physical conditions of metamorphism is uniquely influenced by X_{Mn} and X_{CO_2} , the latter

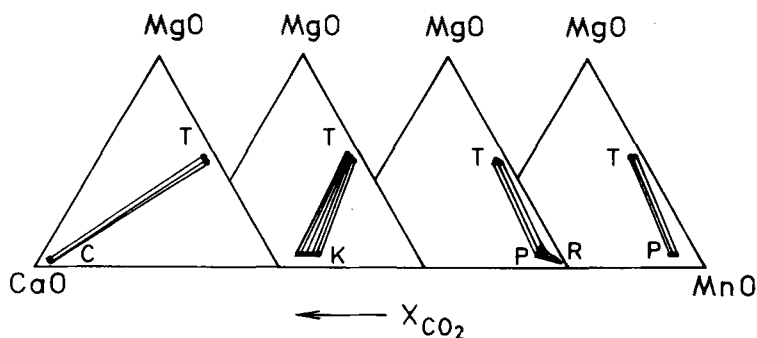


FIG. 2. Composition of the coexisting phases in MgO-CaO-MnO space (projected from H_2O , CO_2 and SiO_2). The diagram shows schematically the behaviour of the tie lines with increasing X_{CO_2} . The triangles from right to left represent assemblages (i) to (iv). T = Tirodite, P = Pyroxmangite, R = Rhodochrosite, K = Kutnahorite and C = Calcite.

being externally monitored in the present situation. It also shows that depending on the ambient f_{O_2} during amphibolite facies metamorphism, the bivalent cations available for the formation of the Mn silicates in the studied rocks were mainly Mn and Mg.

Petrological implications

This study of natural assemblages indicates that under the high f_{O_2} conditions generally existing during metamorphism of Mn silicate-carbonate-oxide protomylonites (cf. Huebner, 1967). Fe cannot influence the stability of the phases containing divalent cations. Further, physical conditions of metamorphism *per se* do not exert the entire control, as wide stability of the Mn silicate phases is exhibited from greenschist to high amphibolite facies rocks (cf. Huebner, 1967; Peters *et al.*, 1980).

It is further revealed that the Mn silicates in the Sausar Group of rocks evolved where the available bivalent cations were mainly Mn and Mg. The X_{Mn} in such situation varied from below 0.3 to 0.4. This is directly relevant, but not identical, with Huebner's (1986) synthesis of phases along the join $MnMgSi_2O_6$ and the suggested phase relations through an isobaric section (Fig. 8 in Huebner, 1986). The appearance of tironite as the sole Mn silicate in assemblages (iii) and (iv) from a bulk composition with $X_{Mn} < 0.3$ at 600–650 °C in our study is consistent with Huebner's experimental data. But both amphibole and pyroxmangite appeared in assemblages (i) and (ii) with $X_{Mn} > 0.35$ under identical physical conditions of metamorphism, instead of Opx/Cpx plus quartz as depicted in Huebner (1986). This is obviously related to low and unbuffered X_{CO_2} in the fluid phase during amphibolite facies metamorphism that will inhibit the development of pyroxenes. Thus, this study demonstrates that the stability of pyroxmangite is considerably extended under high X_{H_2O} in the fluid phase and this is consistent with the experimental data of Peters (1971).

The coexistence of Mn–Mg amphibole, pyroxmangite and Cpx in the Tatehira deposit, Japan (Kobayashi, 1977), may be discussed in this context. Experimental curves of Peters (1971) show that the stability of pyroxmangite is rather insensitive to X_{CO_2} at high temperature (> 500 °C) and low pressures (2 kbar). It is likely that the Tatehira hornblende hornfels facies metamorphism produced Cpx, pyroxmangite and Mn–Mg amphibole in a higher X_{CO_2} regime.

The nature of partitioning of Ca between coexisting Mn-pyroxenoid and carbonates also merits discussion. Winter *et al.* (1981) and Peters *et al.* (1977) described the coexistence of very low calcic

pyroxenoids with very high calcic carbonates. Winter *et al.* (1981) considered it as an 'anomalous' partitioning and related this to a general effect of moderate grades of metamorphism. The results of the present study demonstrate that the stability of pyroxmangite depends on both X_{Mn} and X_{CO_2} of a system, and the phase has an antipathetic relationship with Ca-rich carbonates in X_{CO_2} unbuffered assemblages. The 'anomalous' partitioning of Winter *et al.* (1981) may then be correlated to low to intermediate but buffered X_{CO_2} of the fluid phase rather than to the physical condition of metamorphism.

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