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Two morphologies of pyrophanite in Mn-rich assemblages, Gangpur Group, India

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ABSTRACT

Pyrophanite is widely distributed in metamorphic Mn-rich rock assemblages of the Gangpur Group, India. It occurs in two distinct habits: as an independent phase, and as an exsolved phase within hematite. The well developed large sized crystals coexist with spessartine in Mn-silicate facies rocks. In contrast, the exsolved crystals occur as fine needle/bleb-like crystallites intergrown with hematite in Mn-silicate-oxide facies rocks. Compositionally the exsolved crystals are enriched in iron, present in both the ferric and ferrous states. The two morphologies of pyrophanite attest to their formation under different environmental conditions. The independent pyrophanite is formed from a Mn-Ti rich precursor under low oxygen fugacity conditions while the hematite-pyrophanite intergrowth evolved from an Fe-Mn-Ti rich precursor under higher f_{O_2} conditions.

KEYWORDS: pyrophanite, manganese deposits, hematite, Gangpur Group, India.

Introduction

THE Precambrian Gangpur Group of rocks, India, constitute a volcanic-free, syn-sedimentary sequence metamorphosed to amphibolite facies. The Gangpur Group is well known for its manganese-rich ore bodies that are interstratified with Mn-silicate rocks (Roy, 1966; 1981). Supergene alteration processes enriched the manganese concentration and formed these units into workable deposits.

The manganese-rich rocks of Goriajhar, Sundargarh district, Orissa, have so far been considered as Mn-silicate rocks or gondites (Fermor, 1909; Roy, 1981; Nicholson *et al.*, 1994). However, recent studies by Nayak *et al.* (1997) established that the Mn-rich rocks may be broadly grouped into four major facies: Mn-oxide ores; Mn-silicate rocks; Mn-silicate-oxide rocks; and Mn-silicate-carbonate-oxide rocks. The supergene Mn-oxyhydroxide minerals, which form the major volume in the Mn-rich ores, are however, not included in this scheme of classification. Pyrophanite, a Ti-bearing manganese oxide mineral ($MnTiO_3$), closely associated with some of these assemblages, is reported here from the Gangpur Group of rocks for the first time. But pyrophanite in the Eastern Ghats Group (Rao *et al.*, 1994) and Sausar Group (Dasgupta *et al.*, 1984) from India, in a similar geological set up to the present area, have been reported earlier in Mn-rich parametamorphites. However, pyrophanite and pyrophanite-rich ilmenite are also identified in a wide variety of geological environments (Mucke and Woakes, 1986). In all these cases, this association is reported with high-temperature magmatic events.

This paper describes the diagnostic properties of the Gangpur pyrophanite in terms of its textural peculiarities, morphology, mineral chemistry and paragenesis and correlates its characteristics with pyrophanites reported in Mn-rich metamorphosed rocks from other parts of the world.

Geological setting and mode of occurrence

Pyrophanite occurs as a constituent of Mn-silicate and Mn-silicate-oxide rock assemblages in the Goriajhar region, Sundargarh district, Orissa, India (Fig. 1). The Mn-rich rocks/ores in this area are enclosed by the pelitic Goriajhar Formation of the Gangpur Group (1700–2000 Ma). Pyrophanite along with its coexisting Mn-rich minerals are conformably interstratified with

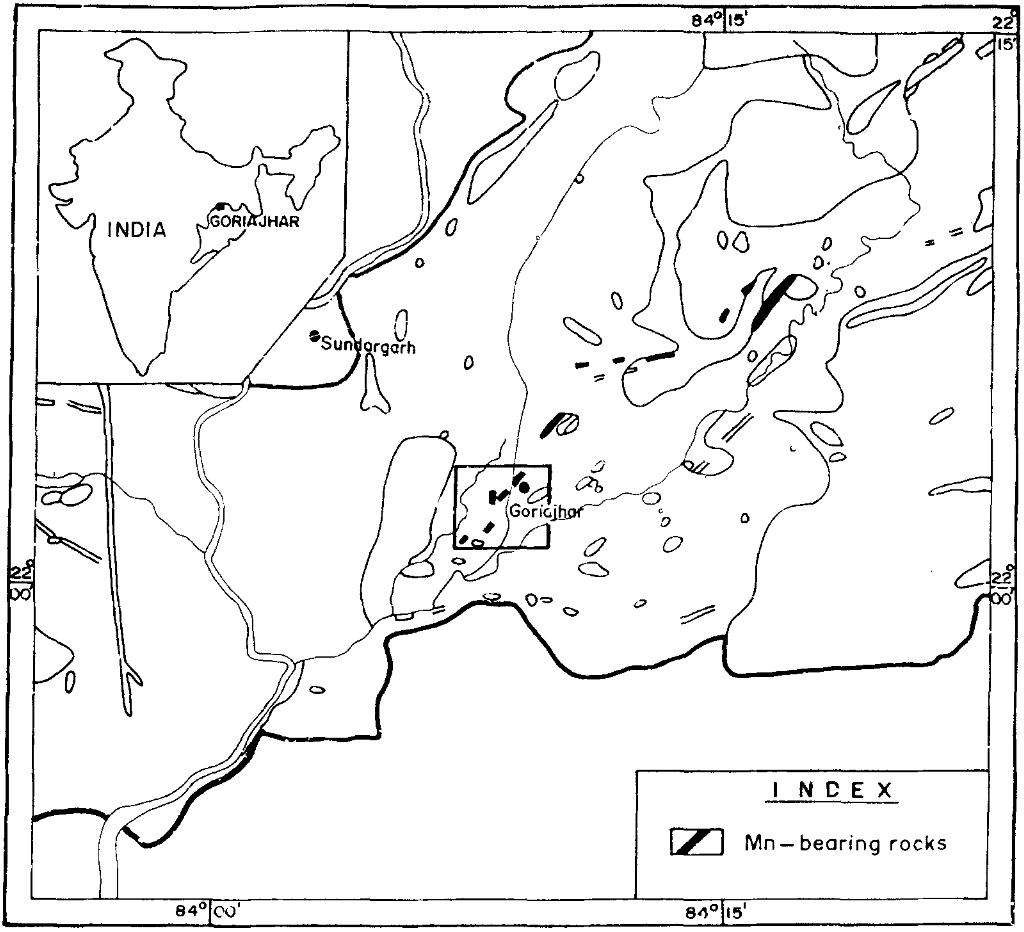

FIG. 1. Outline map of a part of Gangpur Group, India, showing location of Goriajhar and disposition of Mn-bearing rocks/ores.

phyllites, mica schists and metacherts and show an imprint of an identical metamorphic history (850 Ma). These manganese-rich assemblages are considered as analogous to those of the Precambrian Sausar Group of rocks in the Madhya Pradesh and Maharastra regions of India (Roy, 1981).

Texture and morphology

Pyrophanite generally occurs in the following two major assemblages. It mostly appears as an accessory species in Mn-rich rocks/ores and occupies 1–4% by volume. The other co-existing members in the associations are:

1. Mn-silicate facies: (i) pyrophanite + spessartine + quartz
2. Mn-silicate-oxide facies: (ii) pyrophanite + spessartine + rhodonite + hematite; (iii) pyrophanite + spessartine + pyroxmangite + magnetite; (iv) rhodonite + tirodite + hematite (+pyrophanite exsolved).

Most of the literature describes pyrophanite as a rare mineral species, though its occurrence as an independent phase has also been reported (Ramdohr, 1969; Craig *et al.*, 1985; Mucke and Woakes, 1986; Rao *et al.*, 1994). Pyrophanite in the Gangpur Group of rocks, occurs in two different states, either as a distinct independent phase, or as an exsolved phase. The former type

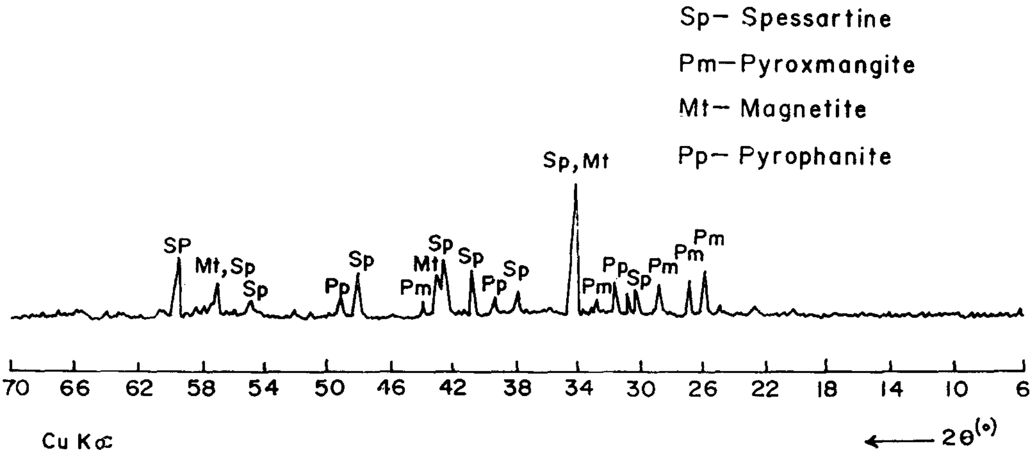

FIG. 2. X-ray diffraction pattern of a pyrophanite-bearing assemblage [association 2(iii)].

exhibits various habits, such as: (i) disseminated grains, (ii) clusters showing mosaic texture, (iii) intergrown with spessartine, and (iv) inclusions within magnetite and spessartine. The second type mostly appears as oriented lamellae and blebs exsolved within hematite. Mn-rich rocks containing spessartine (associations i–iii) usually contain the independent type, while in association (iv) pyrophanite appears mostly as oriented intergrowths within hematite. Figure 5 illustrates the

TABLE 1. Electron probe micro-analyses (EPMA) of pyrophanite

	1	2	3	4	5	6
FeO	6.74	5.95	9.49	4.13	2.33	3.06
TiO_2	50.73	49.59	50.32	52.99	53.41	53.96
MnO	41.45	43.53	39.20	41.51	44.34	43.21
FeO(c)	3.63	0.47	5.57	4.13	2.33	3.06
Fe_2O_3(c)	3.46	6.09	4.36	–	–	–
Cr_2O_3	–	–	0.06	–	0.09	0.13
Total	99.27	99.68	99.51	98.63	100.17	100.36
On the basis of 2 cations						
Ti	0.967	0.942	0.958	1.016	1.007	1.017
Mn^{2+}	0.890	0.932	0.840	0.896	0.942	0.917
Fe^{2+}	0.077	0.010	0.118	0.088	0.049	0.064
Fe^{3+}	0.066	0.116	0.083	–	–	–
Cr	–	–	0.001	–	0.002	0.002
Pyrophanite	89.0	93.2	84.0	89.6	94.2	91.7
Ilmenite	7.7	1.0	11.8	8.8	4.9	6.4
Eskolaite	–	–	0.1	–	0.1	0.2
Hematite	3.3	5.8	4.1	–	–	–
Excess Ti	–	–	–	1.6	0.8	1.7

(c): calculated value
1–3: exsolved phases
4–6: independent phases

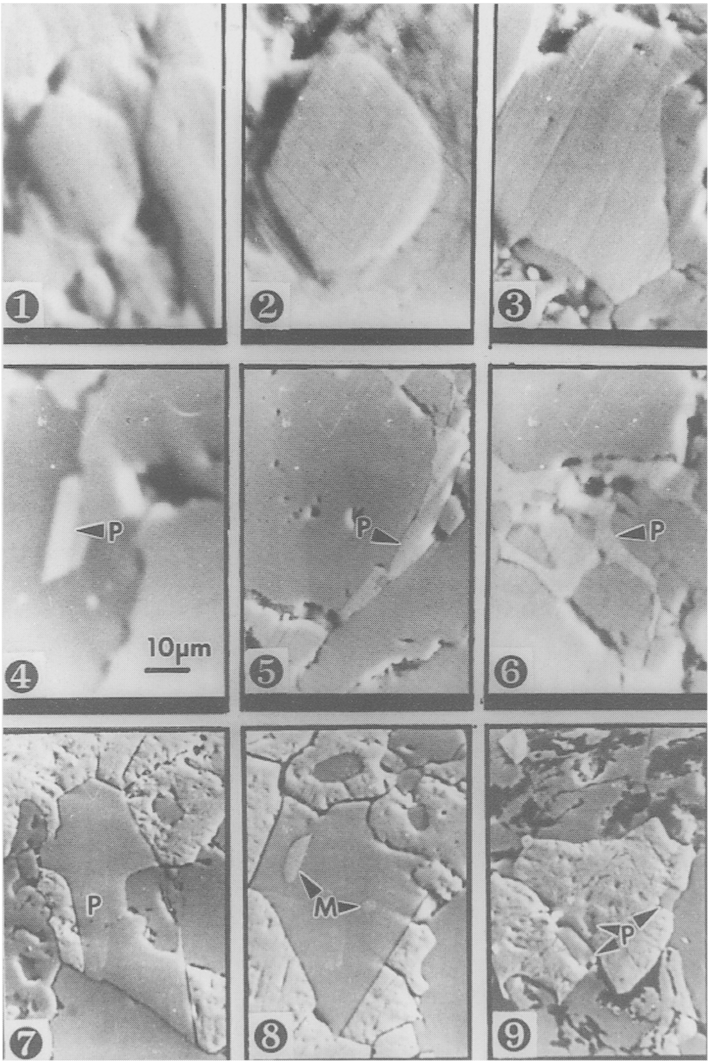

FIG. 3. Scanning electron micrographs of pyrophanite crystals in different habits: (1) Well developed hexagonal crystal; (2) rhombohedral crystal; (3) subhedral crystal; (4) prismatic crystal (P); (5) elongated grain developed in the intergranular spaces; (6) irregular grain (P), all associated with other silicate minerals (darker grey); (7) wedge shaped pyrophanite (P) bordered by both magnetite (top) and silicate (bottom); (8) subhedral pyrophanite containing inclusion of magnetite (M); and (9) magnetite containing inclusions of pyrophanite (P).

oval drops of pyrophanite aligned like a string of beads within the host hematite. In Mn-ores that have suffered supergene alteration, independent pyrophanite crystals occur as relics within a vernadite/nsutite/cryptomelane base (Fig. 4).

Most of the pyrophanite grains exhibit a distinct crystal outline, some being perfectly euhedral. These grains occur in variable sizes (from 1 μm to over 0.1 mm), exhibiting habits such as well developed hexagonal crystals (Fig. 3.1), rhombohedral crystals (Fig. 3.2), subhedral crystals (Fig. 3.3), fine prismatic crystals (Fig. 3.4), elongated grains along intergranular spaces (Fig. 3.5), in irregular shape

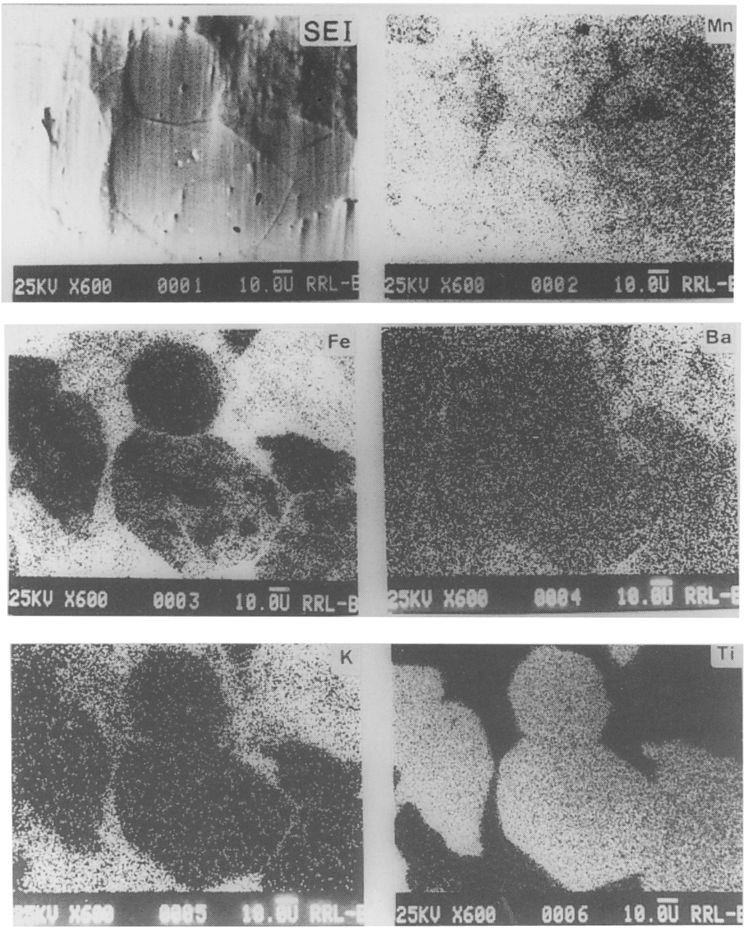

FIG. 4. Scanning electron micrograph showing secondary electron image (SEI) of pyrophanite crystals and vernadite with X-ray image maps of Mn, Fe, Ba, K and Ti.

within grain boundaries (Fig. 3.6), wedge shaped crystals (Fig. 3.7) and minute inclusions within magnetite (Fig. 3.9). Often pyrophanite encloses small inclusions of hematite or magnetite (Fig. 3.8).

Mineralogy

Pyrophanite in the Gangpur Group appears as a distinct species. It has a bluish-grey colour, rarely with a brownish tinge and is highly bireflectant in grey and brownish-grey shades. The anisotropism is strong in grey, bluish-grey, brown and slate blue colours. Almost all pyrophanite crystals show well defined brick-red internal reflections. The microhardness values (VHN_{50}) measured, vary from 531 to 693 kg/mm^2. The XRD pattern of one assemblage where distinct reflection peaks of pyrophanite are marked is shown in Fig. 2.

The distinctive properties of exsolved pyrophanite, observable under optical microscope as fine striations within hematite, could not be recorded owing to their size limitations.

Mineral chemistry

Chemical compositions of pyrophanite in the two assemblages were determined by an ARL-SEMQ-II electron microprobe in the Geochemisches Institut, Universitat Gottingen, Germany, which is equipped with six spectrometers and four different crystals. The operating conditions were 15 kV accelerating voltage and 15 nA sample current. ZAF-corrected representative mineral analyses are presented in Table 1.

From the electron probe micro-analytical results it is noticeable that pyrophanite has TiO_2 49.59–53.96 wt.% and MnO 39.2–44.34 wt.%. A maximum of 0.13 wt.% Cr_2O_3 is occasionally recorded. All crystals analysed have a considerable amount of iron. X-ray image maps (Fig. 4) show that, (i) pyrophanite contains minor amount of barium in solid solution (around 0.3%), and (ii) iron is irregularly distributed.

The independent pyrophanite crystals have a low iron concentration (FeO^t: 2–4 wt.%) and the compositional range is equivalent to a formula of $(Mn_{0.89-0.94}Fe^{2+}_{0.04-0.08})(Ti_{1.00-1.01})O_3$. The exsolved bodies have relatively higher iron concentration (FeO^t: 5–9 wt.%), Fe being present both in ferrous and ferric states (Table 1), and correspond to the formula $(Mn_{0.84-0.93}Fe^{2+}_{0.01-0.11}Fe^{3+}_{0.06-0.11})(Ti_{0.94-0.96})O_3$. The host hematite in hematite–pyrophanite pairs also contain both manganese (MnO^t: 1.90–2.49wt.%) and titanium (TiO_2: 1.14–1.60 wt.%), which correspond to the formula $(Fe_{1.91-1.92}Mn_{0.04-0.05}Ti_{0.02-0.03})O_3$ (Table 2).

Discussion

Pyrophanite has an ilmenite-type structure (Lindsley, 1981) and forms an end-member of the ternary solid-solution system Fe_2O_3–$FeTiO_3$–$MnTiO_3$. With the introduction of a considerable amount of Mn into the ilmenite structure, pyrophanite is formed. Besides the major elements Mn and Ti, other elements such as Fe, Mg, Si, V, Al, Ca, Ba and Co have also been reported to occur in minor and trace amounts in pyrophanite. Sivaprakash (1980) reported the presence of SiO_2 (0.34–0.56 wt.%), V_2O_3 (0.14 wt.%) and FeO (1.51–1.78 wt.%) in pyrophanite from Koduru and Garbham, Andhra Pradesh, India. Alumina (Al_2O_3: 0.05 wt.%) and calcium (CaO: 0.07 wt.%) in pyrophanite from Chikla area, Sausar Group, India have been recorded by Dasgupta *et al.* (1984). Rao *et al.* (1994) noted MgO (0.031 wt.%), BaO (1.31 wt.%) and CoO (0.037 wt.%) in pyrophanite from Nishikhal manganese deposit, Eastern Ghats, India.

Goriajhar pyrophanites almost attain the composition of the end-member (84–95%) with minor mol.% of ilmenite (1–12%) and hematite (3–6%) components. From the triangular plot MnO–TiO_2–FeO (Fig. 6), it is apparent that the Goriajhar pyrophanite is compositionally similar to that of six other manganese deposits located in different parts of the world, and forms within the naturally occurring compositional zone of the ilmenite–pyrophanite join. However, pyrophanite from Mn-rich assemblages of the Nishikhal deposits, India (Rao *et al.*, 1994) departs from the composition of that of Goriajhar since it contains 17 wt.% FeO. When all these pyrophanite analyses (plotted in Fig. 6) are superimposed on the tetrahedral diagram (the system $FeTiO_3$–$MnTiO_3$–$MgTiO_3$–Fe_2O_3) of the rhombohedral phases (Haggerty, 1976), an independent well defined field is obtained (Fig. 7). Pyrophanite occurrences in Mn-rich metamorphites of the Gangpur Group, India, thus acquire a separate status, which is distinctly different from those

TABLE 2. Electron probe micro-analyses (EPMA) of host hematite in hematite–pyrophanite pairs

	1	2	3
MnO	2.31	2.49	1.90
FeO	86.64	86.39	87.21
CaO	–	–	0.29
TiO_2	1.45	1.60	1.14
Al_2O_3	–	–	–
MnO(c)	1.29	1.42	0.66
Mn_2O_3 (c)	1.14	1.19	1.38
FeO(c)	–	–	–
$Fe_2O_3$3(c)	96.29	96.01	96.93
Total	100.17	100.22	100.40
On the basis of 2 cations			
Ca	–	–	0.008
Ti	0.029	0.032	0.023
Al	–	–	–
Mn^{2+}	0.029	0.032	0.015
Mn^{3+}	0.023	0.024	0.028
Fe^{2+}	–	–	–
Fe^{3+}	1.919	1.912	1.926
$CaTiO_3$ End mb.	–	–	0.80
Pyrophanite	2.90	3.20	1.50
Mn_2O_3 (Th)	1.15	1.20	1.40
Hematite	95.95	95.60	96.30

(c): calculated value
(Th): theoretical value

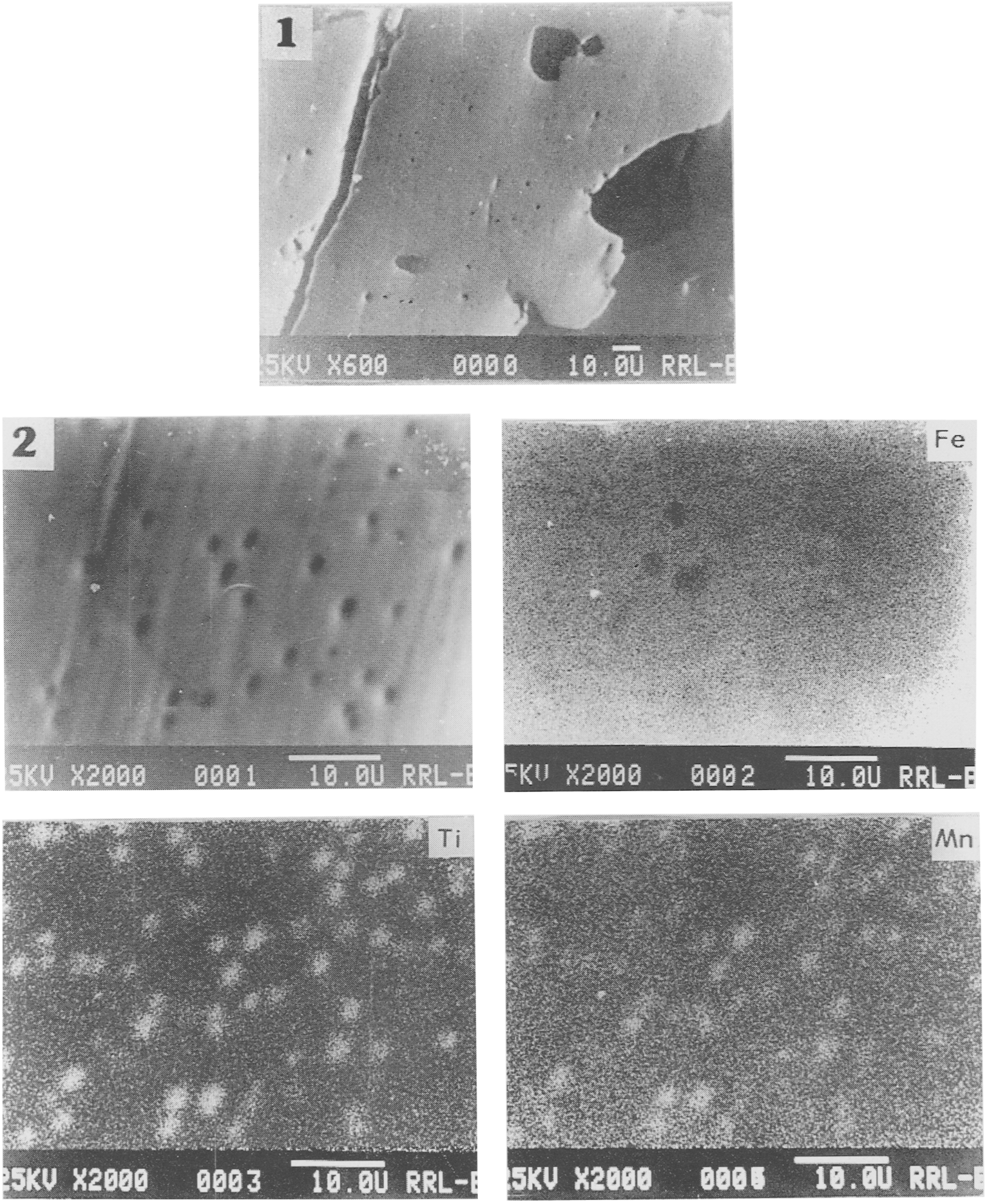

FIG. 5. (1) Secondary electron image of hematite with exsolutions of pyrophanite (small spots). (2) An enlarged view of the above figure showing oval drops of pyrophanite resembling a string of beads. The other micrographs are the X-ray image maps of Fe, Ti and Mn in the area shown in (2).

having a magmatic affinity (pegmatite/kimberlite/carbonatite/anorthosite).

Pyrophanite is a product of high-grade metamorphism and may form from a Mn- and Ti-rich protolith. However, it may have two morphological associations, either as independent grains or as exsolved phases, suggesting different conditions of formation. The occurrence of

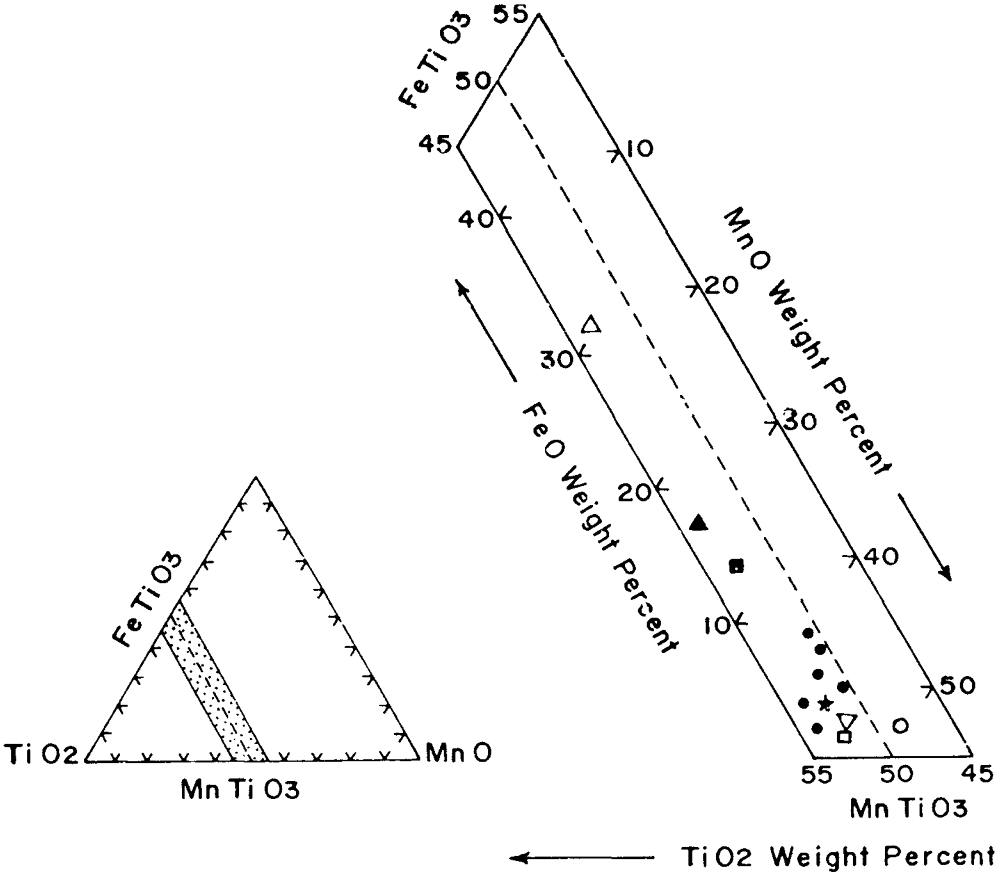

FIG. 6. Compositional plots of Goriajhar pyrophanites (closed circles) and from other deposits. Open circle: Chikla, Sausar Group, India (Dasgupta *et al.*,1984); closed triangle: Nishikhal, Eastern Ghats, India (Rao *et al.*, 1994); open square: Kodur, Eastern Ghats, India (Sivaprakash, 1980); open inverted triangle: Sterling Hill, New Jersey (Craig *et al.*, 1985); star: Chvaletice, Bohemia (Zak, 1971); open triangle: Australia (Simpson, 1929; cited in Palache *et al.*, 1944).

pyrophanite as well developed crystals in a spessartine association is indicative of the original precursor being Mn- and Ti-rich. This is evident from the 0.07–0.56 mol.% of schorlomite component in the coexisting spessartine member. This pyrophanite structure with a dominance of Mn^{2+} is probably formed at low- to average-f_{O_2}, since it is earlier reported (Haggerty, 1976) that Mn^{3+} could stabilise at high values of f_{O_2}.

In the Mn-silicate-oxide assemblage pyrophanite occurs either as inclusions (10–20 μm) or as fine oriented blebs within hematite. Similar intergrowth textures between hematite and pyrophanite have been reported in the Sausar Group of rocks, Maharastra, India (Dasgupta *et al.*, 1984) and jacobsite-pyrophanite in Koduru-Garbham deposit, Andhra Pradesh, India (Sivaprakash, 1980). These types of pyrophanites are formed from a Fe-, Mn- and Ti-rich protolith. Crystallographically oriented intergrowth of Goriajhar pyrophanites with hematite attests to their formation through exsolution and not by guided replacement. This is supported by: (i) the blebs occur oriented in the hematite host nearly parallel to the 001 plane; (ii) Ti and Mn in the hematite grains, though in low concentration, are uniformly distributed and; (iii) the oriented blebs show enriched Mn and Ti content (Fig. 5).

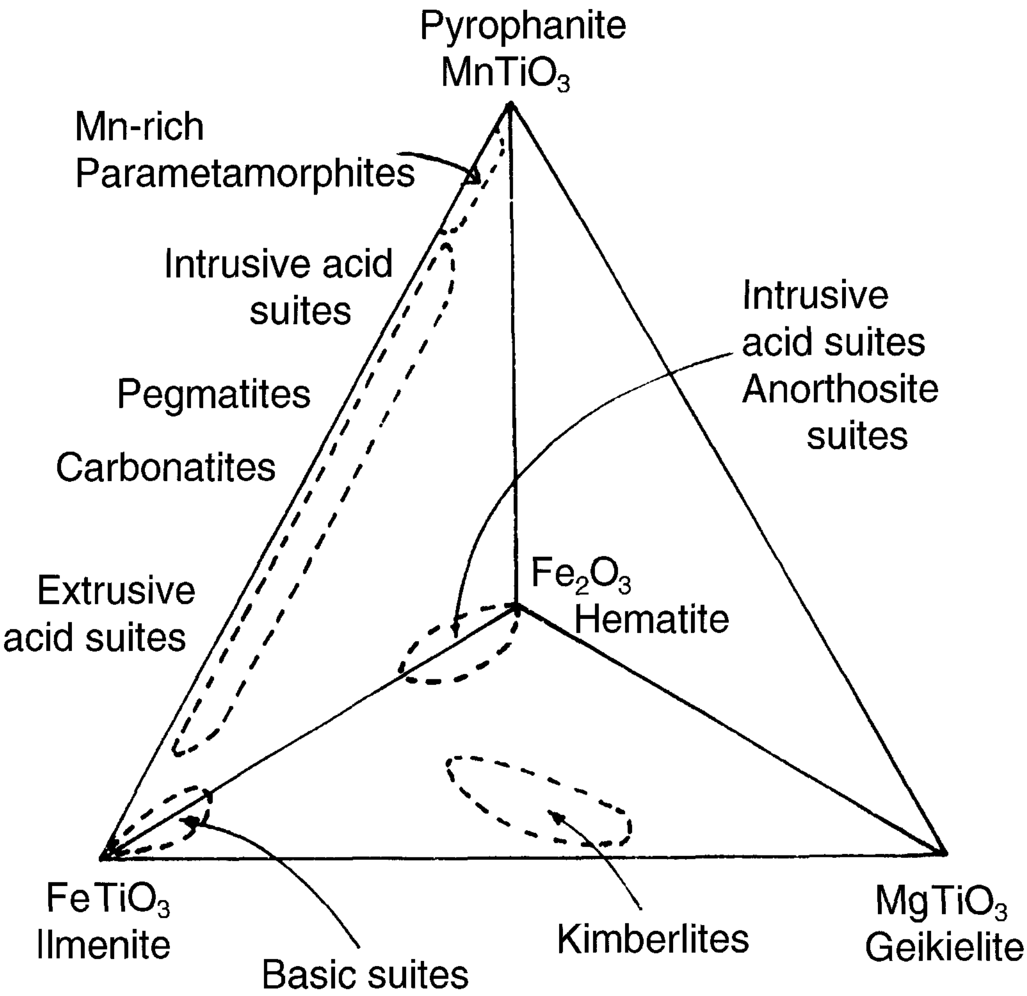

FIG. 7. Generalised distribution of rhombohedral phases in the quarternary system $FeTiO_3$–$MnTiO_3$–$MgTiO_3$–Fe_2O_3 (after Haggerty, 1976). The proposed field of Mn-rich metamorphites has been superimposed on the system.

This clearly reveals that hematite-pyrophanite pairs were formed by exsolution from an original hematite, which contained Mn and Ti in solid solution. The exsolution is attributed to the cooling history. At high temperatures the homogeneously distributed Mn and Ti in hematite become exsolved into pyrophanite with decreasing temperature. This suggests that Mn is preferentially taken up within an ilmenite-type structure rather than that of hematite. The partitioning of MnO into ilmenite structure may have been effective with decreasing temperature below 700°C as suggested by Anderson (1988) and Lindsley (1991). An average of 2.2 wt.% MnO (1.90–2.49 wt.%) and 1.4 wt.% TiO_2 (1.14–1.60 wt.%) is recorded in hematite adjacent to pyrophanite blebs. The hematite–pyrophanite pairs may well have formed in areas of average to high f_{O_2}. The anhedral inclusions of pyrophanite within hematite (Fig. 3.9) may be a local development of the exsolved phase due to post-exsolution grain boundary equilibration in attaining lower interfacial energy (Craig and Vaughan, 1981).

Conclusions

Pyrophanite in Mn-rich rocks of the Gangpur Group, India, exhibits two contrasting habits. Independent euhedral to subhedral grains, in larger grain-size ranges, occur preferentially in Mn-silicate facies rocks rich in spessartine, while fine oriented blebs mostly appear as an exsolved phase within hematite in the Mn-silicate-oxide rock assemblage. This dual occurrence of Goriajhar pyrophanite may be attributed to variations in the proportions of metallic elements in the precursor and local differences in the oxygen fugacity condition during metamorphism. However, the pyrophanite, being a resistant mineral, is little affected by lateritization and in most cases occurs as relics within tetravalent Mn-oxide rich matrices (vernadite/nsutite/cryptomelane).

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