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Hematite-pyrophanite intergrowth in gondite, Chikla area, Sausar Group, India

PYROPHANITE (MnTiO₃, ilmenite-type structure; Lindsley, 1981) has been reported as a minor constituent of some metamorphosed manganese deposits (Lee, 1955; Zak, 1971; Sivaprakash, 1980) and exsolution lamellae of pyrophanite in jacobsite (Sivaprakash, 1980) and in magnetite and franklinite (Ramdohr, 1980, pp. 922, 997) have been described. But there is, as yet, no record of crystallographically oriented intergrowth of pyrophanite and hematite. This paper presents data on the textural relationship and chemistry of pyrophanite and hematite forming such intergrowths in gondites of Chikla area (Maharashtra State, India) in the Precambrian Sausar Group.

The gondites are manganese silicate-oxide rocks produced by metamorphism of manganiferous noncalcareous sediments (Roy, 1966, 1981). This rock occurs in India mainly in the Precambrian Sausar Group. In the Chikla area, the gondites have been metamorphosed to staurolite-kyanite grade as determined from the enclosing cometamorphosed pelites (Mitra, 1965; Roy, 1966). These consist of spessartine, quartz, rhodonite, braunite, jacobsite, hematite, tirodite, apatite, Kfeldspar, and minor pyrophanite. The gondites are interbanded with metamorphosed ferromanganese ores containing braunite, hollandite, hematite, bixbyite/jacobsite and hausmannite and both have identical thermodeformational history (Roy, 1966). Hematite mainly occurs as minute specks in the oxide ores but in gondite it forms coarse subidioblatic grains. The hematite grains in gondite often contain tiny blebs and spindles of pyrophanite arranged along the (0001) plane of the host (fig. 1). Occasionally, however, pyrophanite occurs

as sub-equant grains, but in such cases also it is always confined to the grain limits of hematite.

The chemical composition of coexisting hematite and pyrophanite was determined by Electron Probe Microanalyzer JEOL/JXA-5A model at the Geology Department, Kyushu University, Japan. Carbon-coated surfaces were analysed with accelerating voltage of 15 kV, specimen current of 0.020 μ A and 1 to 2 μ electron beam diameter. The standards used were natural MnO and synthetic CaSiO₃, Fe₂O₃, Al₂O₃, and TiO₂. For matrix correction the Bence and Albee (1968) method was adopted. Beam drifting was checked at regular

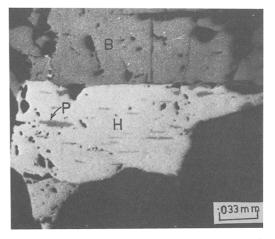


FIG. 1. Blebs and spindles of pyrophanite (P) oriented along the (0001) plane of hematite (H). Associated phases: braunite (B), spessartine and quartz (black).

	1		2		3		4
	Hm	Ру	Hm	Ру	Hm	Ру	Hm
SiO ₂	0.04	0.03	0.06	0.09	0.08	0.06	0.05
TiO ₂	0.96	49.62	1.12	49.69	1.01	49.01	1.85
$Al_2 \tilde{O}_3$	0.03	0.04	0.03	0.04	0.03	0.05	0.01
$Fe_2O_3^*$	96.03	2.17	95.80	1.49	97.38	0.88	96.41
Mn ₂ O ₃ †	1.94	3.16	1.16	2.72	0.56	4.67	0.80
MnO†	0.93	44.01	1.08	44.16	0.96	43.50	1.675
CaO	0.06	0.06	0.07	0.06	0.08	0.07	0.07
Total	99.99	99.09	99.32	98.25	100.10	98.24	100.865
	Numbers	of ions ca	culated or	the basis	of 3(O) per	formula u	unit
Si	0.001	0.001	0.001	0.002	0.001	0.002	0.001
Ti	0.019	0.947	0.022	0.956	0.019	0.944	0.036
Al	0.001	0.001	0.001	0.001	0.001	0.002	
Fe ³⁺	1.918	0.041	1.928	0.029	1.948	0.017	1.905
Mn ³⁺	0.039	0.061	0.022	0.053	0.009	0.091	0.015
Mn ²⁺	0.020	0.946	0.024	0.957	0.020	0.943	0.036
Ca	0.001	0.002	0.001	0.001	0.001	0.002	0.001
Total	1.999	1.999	1.999	1.999	1.999	2.001	1.994

 TABLE I. Composition of hematite (Hm) and pyrophanite (Py) in gondite, Chikla area, Sausar Group, India

In nos. 1, 2, and 3, Hm and Py coexist; in no. 4 Hm is not in contact with Py.

* Total Fe as Fe₂O₃.

† Recalculated from total Mn content.

intervals. In Table I the chemical compositions of pyrophanite and hematite and the cation proportions of these minerals, calculated on the basis of 3(O), are presented. The molecular proportions of these minerals, in terms of the three end members pyrophanite-hematite-bixbyite, are given in Table II. Analysis 4 in Table I is of a hematite grain which is not in physical contact with pyrophanite.

Crystallographic intergrowths of minerals may form by exsolution or by guided replacement. The following observations on hematite and pyrophanite forming the intergrowths in the Chikla gondite are relevant: (a) Pyrophanite occurs as sharply defined blebs and spindles in the hematite host along its (0001) plane; (b) hematite contains variable amounts of the bixbyite and pyrophanite molecules (Table II); and (c) hematite, immediately adjacent to the blebs and spindles of pyrophanite, is depleted in Ti (compare analysis 4 with the rest in Table I). These observations suggest that the hematitepyrophanite intergrowth in the Chikla gondite was formed by exsolution from an original hematite_{ss}. Local development of sub-equant grains of the exsolved phase could be the result of post-exsolution grain boundary equilibration in attaining lower interfacial energy (Craig and Vaughan, 1981).

Rumble (1981) predicted that pyrophanite forms an end member of the ternary solid solution system Fe_2O_3 -FeTiO₃-MnTiO₃ in metamorphic rocks. The metamorphosed manganese deposits of the Sausar Group including those of Chikla, are characterized by the presence of ubiquitous braunite and progressive appearance of reduced phases in a prograde sequence, namely pyrolusite \rightarrow bixbyite \rightarrow hausmannite in the ore assemblages and pyrolusite \rightarrow jacobsite \rightarrow spessartine and/or rhodonite in the gondites (Roy, 1966). Hematite is the

TABLE II. Compositions of coexisting hematitepyrophanite in terms of the components Fe_2O_3 - Mn_2O_3 -MnTiO₃

1.	Hematite: Pyrophanite:	Hm _{95.95} Bx _{1.95} Py _{2.10} Hm _{2.05} Bx _{3.05} Py _{94.90}
2.	Hematite: Pyrophanite:	$\begin{array}{c} Hm_{2.05} & Bx_{3.05} & y_{94.90} \\ Hm_{96.45} Bx_{1.10} Py_{2.45} \\ Hm_{1.45} & Bx_{2.65} Py_{95.90} \end{array}$
3.	Hematite: Pyrophanite:	$\frac{\text{Hm}_{1.45} \text{Bx}_{2.65} \text{Fy}_{5.50}}{\text{Hm}_{97.45} \text{Bx}_{0.45} \text{Py}_{2.10}}$ $\frac{\text{Hm}_{0.85} \text{Bx}_{4.55} \text{Py}_{94.60}}{\text{Hm}_{0.85} \text{Bx}_{4.55} \text{Py}_{94.60}}$

Hematite (Hm); Bixbyite (Bx); Pyrophanite (Py). The serial numbers correspond to those in Table I.

only Fe-oxide phase present in the mineral assemblage of most of the deposits. In the gondite, the assemblage of braunite, jacobsite, and hematite, in the complete absence of magnetite, was obviously stabilized above the Fe₂O₃-Fe₃O₄ buffer. The hematite-pyrophanite pair, therefore, must have equilibrated at high f_{O_2} . The appearance of ilmenite, the generally common associate of hematite in metamorphosed rocks, was therefore inhibited.

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Grimaldiite, CrOOH, a second occurrence, from the Hiaca Mine, Colquechaca, Bolivia

GRIMALDIITE, rhombohedral CrOOH, was first reported by Milton et al. (1967, 1976) from gravels in a small tributary of the Merume River, Guyana. It is there intergrown with eskolaite, Cr_2O_3 , and two other CrOOH polymorphs, guyanaite and bracewellite, both orthorhombic (a synthetic orthorhombic fourth CrOOH polymorph is also known). These water-worn grains and pebble-sized aggregates were first described by Bracewell (1946) as a hydrous chromium (aluminium) oxide 'merumite'; the largest concentration of merumite was in a strip 3-4.5 m wide and 3 km long. Almost all the Guyana grimaldiite is further interleaved with isostructural mcconnellite (CrOOCu); rarely, deepred pure grimaldiite is seen in crushed fragments of merumite. Grimaldiite and mcconnellite are members of the delafossite (FeOOCu) structural group.

A recently purchased small specimen* $(5 \times 3 \times$

2 cm, 79 g) stated to be from the Hiaca Mine some 30 km ENE of Colquechaca, Bolivia (a well-known locality for penroseite (Ni,Co,Cu)Se₂ and cobaltomenite, CoSeO₃ · 2H₂O), contained about 60% penroseite with 40% baryte by volume. An electronprobe microanalysis (three separate spots) of the penroseite gave an average composition Ni 16.1, Co 6.0, Cu 5.7, and Se 72.0, total 99.8%.

The penroseite contains small cracks and cavities, partially coated with a pinkish-brown mineral, at first thought to be cobaltomenite but which X-ray diffraction showed to be grimaldiite, rhombohedral CrOOH; the patterns were identical with that of synthetic rhombohedral CrOOH (Thamer *et al.*, 1957). This is the second discovery of grimaldiite to be reported (M. Fleischer, pers. comm.). It forms radially bladed aggregates of small (0.25 mm) partial spheres or scallop-shaped platy aggregates