

## OCCURRENCE OF PYROPHANITE IN JAPAN

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### ABSTRACT

Pyrophanite, previously reported from only three localities, is widely distributed in Japanese manganese ores. The mineral is present in six of eleven scattered mines that were sampled. Paragenetic associations are summarized and physical, optical, spectrographic and x-ray data are given. Some of the pyrophanite described has an abnormal greenish-yellow color which it is suggested might possibly be due to the presence of minor amounts of cerium.

### INTRODUCTION

Pyrophanite has been previously reported from only three localities. It was originally described by A. Hamberg (1890) who, with G. Flink, found the mineral in drusy cavities in manganese ore at the Harstige mine, Pajsberg, Sweden. The associated minerals are garnet, ganophyllite, "manganophyll," and calcite, the latter having been introduced at a later stage.

Pyrophanite was next reported by A. O. Derby (1901) from the Piquery mine of the Queluz district, Minas Gerais, Brazil, as minute hexagonal grains of a transparent red mineral embedded in garnet and quartz, and he stated; "The crystallographical, optical and chemical characters of this mineral, so far as they can be made out, agree with those of pyrophanite." He describes the quartz as being "abundantly threaded with delicate transparent needles of a white asbestiform mineral."

Later, from the same mine, Derby (1908) reported transparent red grains of a rutile-like mineral which he says gave "strong characteristic reactions for both titanium and manganese." According to Derby, this mineral is associated with a "carbonate (rhodochrosite?), an olivine-like silicate (tephroite)," spessartite, pyrite, ilmenite and occasional rhodochrosite.

The other occurrence of pyrophanite is from the Benallt mine, Rhiw, Carvervanshire, Wales, where W. Campbell Smith (1947) found the mineral associated with pennantite. The identity of this pyrophanite was confirmed by x-ray photographs.

In early 1951 the author, with Dr. C. F. Park, made a reconnaissance survey of a number of small manganese mines in Japan and representative samples were collected from nine mines. In addition the sample and data from the Ajiro mine were furnished by Dr. B. M. Page, and the X-mine specimen studied was supplied by the Department of Mining Engineering, Tokyo University. Pyrophanite was identified in specimens from six mines shown in Fig. 1.

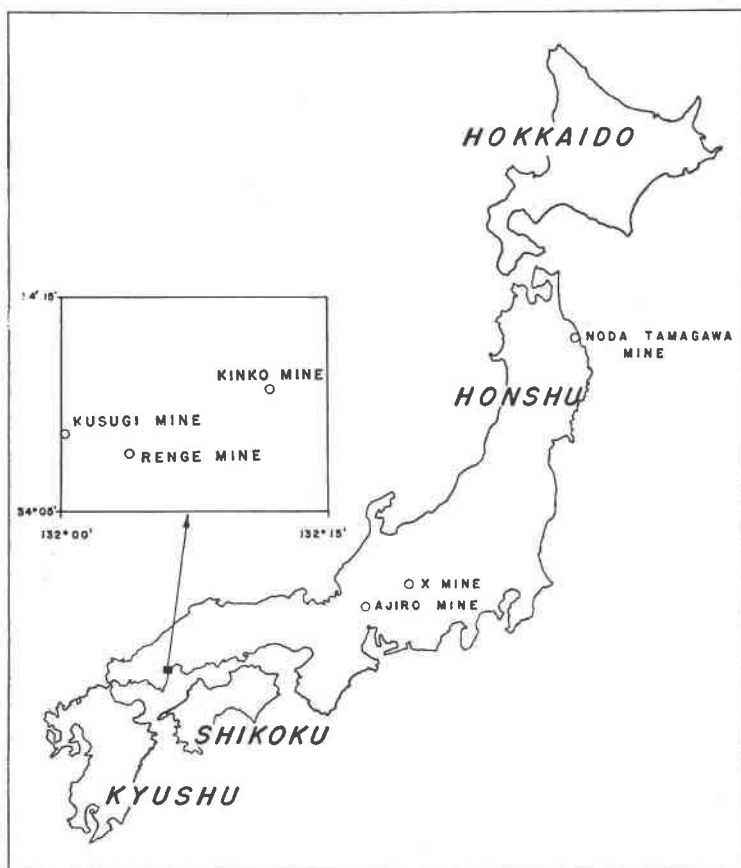


FIG. 1

## ACKNOWLEDGMENTS

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## GENERAL FIELD RELATIONS

Although this paper is not concerned with the genesis of the manganese deposits, a brief summary of available field data will provide a general setting for the minerals described.

Two main types of manganese ores are recognized in Japan. Tertiary

mesothermal fissure-filling deposits, mostly confined to the Oshima Peninsula in southwest Hokkaido, are grouped as the first type.

Deposits of the second type are associated with what Japanese geologists call the "Chichibu Complex." This "Complex" includes an unknown thickness of largely undifferentiated chert, slate, dark gray-wacke, basic volcanic or intrusive rocks, limestone and dolomite. The oldest known rocks in the "Complex" are Silurian whereas the youngest are Permian in age. They were deposited on an unknown basement in a Paleozoic deep off the coast of Asia. Now, more or less metamorphosed, they are distributed in broad areas throughout the four main islands of Japan. The "Complex" contains numerous small manganese deposits which appear to have replaced the chert beds. All specimens described here are from deposits of this kind.

#### PARAGENETIC ASSOCIATIONS

Pyrophanite was found in rocks from the Ajiro, Kinko, Kusugi, Noda Tamagawa, Renge, and X-mines.

(1) *Ajiro mine*.—A mineralized lens in gray chert was being worked. This lens, about two feet thick and 20 feet long, is parallel to, and about three feet from, a healed fault. Thin sections show rhodochrosite, quartz and twinned euhedral pyroxmangite,\* and some evidence points to replacement of the latter by later-introduced carbonate. The small heavy fraction recovered by centrifuging 200-mesh material included grains of alabandite, garnet and greenish-yellow pyrophanite about .03 mm. thick.

(2) *Kinko mine*.—The ore is replacing a chert bed about four feet thick included between beds of graphitic slate, and the workings show clearly an anticlinal structure with limbs dipping about 40°. Minerals seen in thin section are garnet, carbonate, alleghanyite, alabandite, neotocite, pyrophanite and pyroxmangite. The alleghanyite is being replaced, mostly by pyroxmangite, and alabandite exhibits a patchy distribution. Neotocite is characteristically confined to late veinlets. Pyrophanite crystals up to .2 mm. across are often found as inclusions in carbonate or pyroxmangite. Smaller crystals of pyrophanite are concentrated in a few irregular stringers that mark paths of later-introduced material. Pyrophanite ranges in color from blood-red to greenish-yellow, but colors show no relation to crystal size or immediate environment. Rarely does the pyrophanite show any evidence of alteration.

(3) *Kusugi mine*.—The most interesting and significant deposit which was extensively sampled consists of a tabular body in chert of undetermined thickness.

\* It is planned to present data on this and other minerals from this suite in a later paper.

One specimen consists almost entirely of rhodonite through which are scattered small garnet and pyrophanite crystals and rare allanite. Most of the pyrophanite crystals are crimson-red blebs about .003 mm. long, although a few larger crystals are yellowish in color. Other minerals present are neotocite and a very small amount of carbonate.

A second specimen is mainly fine-grained quartz, almost chert-like in some instances. This material is host to allanite, actinolite crystallites, small garnet, apatite grains, tiny blebs of yellow pyrophanite and an opaque mineral with cubic outline. Veinlets of somewhat more coarsely-crystalline quartz criss-cross the finer-grained material as an irregular network. These veinlets are devoid of inclusions except for one euhedral crystal of zoned allanite. Some of the apatite, garnet and pyrophanite is confined to thread-like zones that appear to outline old fracture systems not related to the later network of quartz veinlets. This occurrence is very similar to that described by Derby (1901).

Intergrown pyroxmangite and carbonate are cut by veinlets of later carbonate in the third specimen, and alabandite is associated with both pyroxmangite and carbonate. Other minerals noted are garnet, neotocite, apatite (commonly as inclusions in pyroxmangite), and tephroite. The sparsely-distributed tephroite appears to have been partially replaced by carbonate and pyroxmangite. Garnet and pyrophanite are concentrated in, but not confined to, subparallel bands which may reflect original bedding. Pyrophanite, mostly subhedral, ranges in color from reddish-orange to greenish-yellow and rarely exceeds 0.1 mm. in size. Allanite and monazite were found in crushed material.

Pyroxmangite is the dominant constituent in the fourth specimen with huebnerite, pyrophanite, quartz and an unidentified non-magnetic opaque mineral, all distributed at random in the pyroxmangite. Allanite and barite are rare. Pyrophanite is usually subhedral and, except in one case, is crimson-red in color; the exception occurred as an inclusion in allanite and exhibited a yellowish tint.

(4) *Noda Tamagawa mine*—A deposit about four feet thick is bedded in chert and folded into an overturned syncline. Rhodonite is dominant here and contains stringers of garnet clouded with tiny red pyrophanite blebs. However, larger pyrophanite blebs, up to .003 mm. in diameter, were detected throughout the rhodonite, and exhibit a range of color from crimson-red to yellowish-green. The rhodonite also contains pyrophanite veinlets, the edges of which are yellowish, whereas the central parts are red to orange. Larger veinlets contain later-introduced carbonate, neotocite and bementite (?). Barite, allanite and ilmenite, though present, are not seen in thin section.

(5) *Renge mine*—Chert is the host rock of the deposit and the ore is

concentrated in aligned potato-shaped pods, each up to four yards long. Twinned pyroxmangite makes up most of the sample. Other minerals are garnet, carbonate, neotocite, tephroite, pyrophanite and a ferromagnetic constituent, probably jacobsonite, in small discontinuous fractures in pyroxmangite. The tephroite appears to show alteration to pyroxmangite. Some of the garnet, concentrated in irregular but continuous stringers, has a semi-opaque appearance under low magnification, but with high magnification and intense illumination, myriads of tiny pyrophanite blebs are clearly seen. Pyrophanite in this specimen has a dark blood-red color. Huebnerite also is present, but this was not observed in a thin section.

(6) *X-mine*—The sample is labeled as having come from a skarn zone, and the location suggests that it was obtained from the contact zone between the Chichibu "Complex" sediments and a Mesozoic granodioritic intrusive. The section shows anhedral alabandite in rhodonite. Carbonate, closely associated with the alabandite, often separates it from the rhodonite, and monazite was tentatively identified as inclusions in the silicate. Rhodonite also includes many pyrophanite grains that exhibit a range of color from crimson-red to greenish-yellow. Again, no correlation can be made between color and grain size. One euhedral grain is distinctive for its zoning; a yellowish-orange periphery grades into a red irregularly-shaped inner zone. Apatite, pyrite and galena are present in minor amounts.

#### MINERALOGY

(1) *Form*—Crystals .003 mm. or less in length appear as elongated blebs and show no definite crystal form. The larger crystals have a tabular habit and many of the separated grains show well-developed crystal faces (Fig. 2). Well-developed cleavage planes were occasionally observed.



FIG. 2. *Left*—Yellowish-green crystal of pyrophanite oriented with the dominant face (0001) parallel to the plane of the preparation. Such crystals give centered interference figures and exhibit (11 $\bar{2}$ 0) and (02 $\bar{2}$ 1) cleavages. Locality: Ajiro mine.  $\times 570$ . *Right*—Orange-red crystal of pyrophanite. The euhedral tabular form is typical of many crystals from all six mines described. Interference figure about 5° off center. Locality: Kusugi mine.  $\times 570$ .

(2) *Physical properties*—In oblique illumination pyrophanite has a wine-red color, but when finely ground (powder for x-ray spindle), a dull brownish-green tint is evident.

In transmitted light, color variation from grain to grain is striking, and greenish-yellow and blood-red crystals are often found in the same slide. Zoning within a given crystal is unusual. Colors are not related to crystal size.

Because of their strong preferred orientation perfectly-centered negative interference figures are easily obtained for grains of any color. The ordinary ray has strong positive relief in a sulphur-selenium mount with an index of 2.25.

The largest grains are about .2 mm. long, but the majority are much smaller. This factor and lack of sufficient quantity of the mineral prevented direct specific gravity measurements. It can be stated that pyrophanite here described has a specific gravity greater than that of Clerici at maximum density at room temperature; that is, greater than 4.20.

The red and yellow grains have similar magnetic susceptibility. With the Frantz Isodynamic Separator set at slope 15° and tilt 12°, the smallest grains are drawn off at .2 ampere. Most of the grains are attracted at .25 ampere and at .3 ampere very few remain in the non-magnetic fraction.

Pyrophanite showed no evidence of attack after treatment with 1:1 HCl at 100° C. for one hour.

(3) *Separatory processes*—Crushed material separations served both to isolate as much pyrophanite as possible and to detect the presence of minerals not apparent in thin section.

To insure preparation of monomineralic particles, specimens were broken to pass through 200-mesh bolting silk. Screened material was then freed from dust by repeated washing in a two-liter beaker and decanting until the supernatant water was clear after 90 seconds of particle settling. Turgitol was used to reduce surface tension to a minimum.

In most instances a partial concentration of pyrophanite was effected with the Frantz Isodynamic Separator. Pyrophanite is slightly more paramagnetic than huebnerite, hausmannite or allanite; slightly less magnetic than tephroite or carbonate.

The ability of pyrophanite to withstand acid attack provided a means by which undesired carbonate, neotocite, sulfides and orthosilicates were effectively removed.

Greatest control was achieved with Clerici solution. Of the acid-insoluble minerals with the same range of magnetic susceptibility as that of pyrophanite, only the heavier garnet could not be separated from pyrophanite by centrifuging in Clerici at maximum practicable density (about 4.20).

Hand-picking of pyrophanites was of little use. Most grains are less

than .07 mm. long, and color differences are only apparent in transmitted light with a magnification of over 100 times.

(4) *Spectrographic data*—Qualitative spectrographic analyses were made of two pyrophanite samples.

About three milligrams of mixed red and yellow pyrophanite were isolated from the Kinko mine sample described. The spectrogram shows intense lines for manganese and titanium. Other lines present are those for iron (estimated at less than one per cent), cerium (strong trace), and lanthanum and chromium (traces).

The third sample described from the Kusugi mine yielded about 10 milligrams of material for analysis. About 10 per cent of this preparation

TABLE 1. X-RAY DIFFRACTION DATA FOR PYROPHANITE

POSNJAK AND BARTH			KINKO MINE	
$I-I_1$	$d(\text{\AA})$	$(hkl)$	$d(\text{\AA})^*$	$I-I_1$
30	3.75	110	3.74	10
100	2.78	211	2.76	100
90	2.57	$\bar{1}\bar{1}0$	2.55	70
50	2.25	210	2.25	40
—	2.18	200		
70	1.89	220	1.88	60
80	1.745	321	1.74	70
10	1.655	$\left\{ \begin{array}{l} 332 \\ 2\bar{1}1 \end{array} \right\}$	1.66	5
70	1.518	310	1.52	50
60	1.480	$\bar{2}11$	1.48	50
—	1.388	$\left\{ \begin{array}{l} 300 \\ 22\bar{1} \end{array} \right\}$	1.36	5
40	1.357	$\left\{ \begin{array}{l} 432 \\ 433 \end{array} \right\}$	1.35	10
20	1.280	220	1.28	5
10	1.200	442	1.20	5
10+	1.129	420	1.130	10
20	1.086	$\left\{ \begin{array}{l} 522 \\ 532 \end{array} \right\}$	1.089	20
10—	1.058	$\left\{ \begin{array}{l} 400 \\ 430 \end{array} \right\}$	1.063	5
10	1.010	$\left\{ \begin{array}{l} 3\bar{2}1 \\ 521 \end{array} \right\}$	1.016	10
		$\left\{ \begin{array}{l} 531 \\ 41\bar{1} \end{array} \right\}$		
10	.970	$\left\{ \begin{array}{l} 321 \\ 511 \end{array} \right\}$	.982	10

\* Fe filtered with Mn.  $\lambda=1.9373 \text{ \AA}$ . Camera radius 57.3 mm.

was garnet; the remainder was pyrophanite, some red, some yellow. Lines for manganese and titanium are again intense. Other elements in evidence are silicon, aluminum, magnesium, iron (estimated at less than two per cent), cerium (trace) and vanadium (weak trace).

(5) *X-ray diffraction data*—A complete and accurate set of diffraction data were obtained only for the Kinko mine pyrophanite. As noted, this pyrophanite ranges in color from blood-red to greenish-yellow. Results are compared with the data of Posnjak and Barth (1934) in Table 1. Intensities listed for the Kinko pyrophanite are visual estimates only.

For the three largest  $d$  spacings the Kinko pyrophanite has values consistently lower than those listed by Posnjak and Barth. Moreover, the very weak (200) line recorded was not apparent on the Kinko film. However, except for those discrepancies, the two sets of values are in close agreement.

The lines on the Kinko film are sharp, with no suggestion of doublets. Thus the cell sizes for red and yellow varieties do not appear to be significantly different.

#### CONCLUSION

The widespread presence of pyrophanite in these "ores" should be viewed in the light of the low over-all iron content of the associated minerals; analytical and spectrographic data indicate that most of these specimens contain less than one per cent iron. Nevertheless, pyrophanite is probably a much more common mineral than previously supposed. In thin section it may easily be mistaken for rutile or priderite (Norrish, 1951); indeed, it was not until a casual check was made of the optic sign of freed crystals that pyrophanite was suspected in these samples.

Though Derby was unable to check his determinations with  $x$ -ray diffraction work, the similarity of occurrence of his reported pyrophanites with some of those described here would seem to offer circumstantial evidence in support of his results.

The compositional change reflected in the color range of these pyrophanites cannot of course be known until analyses of the red and the greenish-yellow concentrates are available. Pending such analyses, it is suggested that the greenish-yellow color of some of the pyrophanite might be due to the presence of small amounts of cerium.

#### REFERENCES

- DERBY, A. O. (1901), On the manganese ore deposits of the Queluz (Lafayette) District, Minas Geraes, Brazil: *Am. Jour. Sci.*, Ser. 4, 12, 18-32; esp. p. 21.  
— (1908), On the original type of the manganese ore deposits of the Queluz District, Minas Geraes, Brazil: *Am. Jour. Sci.*, Ser. 4, 25, 213-216; esp. p. 215.



- HAMBERG, A. (1890), Über die Manganophylle von der Grube Harstigen bei Pajsberg in Vermland: *Geol. För. Förh.*, Stockholm, **12**, 567-637, esp. pp. 598-604, 632.
- NORRISH, K. (1951), Priderite, a new mineral from the leucite-lamproites of the west Kimberly area, Western Australia: *Mineral. Mag.*, **29**, 496-501.
- POSNJAK, E., AND BARTH, T. F. W. (1934), Notes on some structures of the ilmenite type: *Z. Krist.*, **88**, 271-280.
- SMITH, W. CAMPBELL, AND CLARINGBULL, G. F. (1947), Pyrophanite from the Benallt mine, Rhiw, Carnarvonshire: *Mineral. Mag.*, **28**, No. 187, 108-110.

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